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Preparation and Characterization of a Novel β-Cyclodextrin Modified Poly(*N*-acetylaniline) Film

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ABSTRACT: Hydroquinone was chosen as an electroactive probe to study the β-cyclodextrin (β-CD) modified poly(*N*-acetylaniline) (PNAANI) electrode. The β-CD modified PNAANI electrode was prepared by electrooxidation of the PNAANI electrode in a β-CD/DMSO solution. The electrochemical properties of the β-CD inclusion complex of hydroquinone on the PNAANI electrode and hydroquinone on the β-CD modified PNAANI electrode were studied. In the cyclic voltammogram of hydroquinone at the β-CD/PNAANI electrode, ΔE_p of the peaks is sharpening and the area of the peaks is increasing, which can be due to the inclusion of hydroquinone into the cavity of β-CD immobilized at the electrode surface. The β-CD/PNAANI film was characterized by X-ray photoelectron spectroscopy and ^{1}H NMR. The mechanism for β-CD incorporation into the polymer film was also proposed.

1. Introduction

Polyaniline (PANI) is one of the most extensively studied conducting redox polymers[1,2] due to its potential applications in lithium batteries,[3] electrochromic devices,[4] electrochemical supercapacitor materials,[5,6] immobilization of enzyme,[7] etc. Although PANI is one of the more stable conducting polymers, highly oxidized conducting polymers are prone to nucleophilic degradation by water.[8] Other nucleophiles readily attack and incorporate into the oxidized PANI, too.[8,9]

Cyclodextrins are oligosaccharides consisting of six, seven, or eight glucose units (named α, β, or γ-CD, respectively) which present a toroidal form with a hydrophobic inner cavity and a hydrophilic outer side.[10] This property is in favor of forming inclusion compounds with a large variety of organic molecules, which has led to many applications in organic chemistry,[11] electrochemistry,[12,13] and the pharmaceutical field.[14]

In the present paper, we report a novel approach of preparing β-CD modified poly(*N*-acetylaniline) film electrode by electrooxidation of PNAANI film in β-CD solution. The hydroxy group of β-CD, which acts as nucleophile, can be attached to the polymer backbone. An electroactive probe, hydroquinone, is selected to study the β-CD/PNAANI film since the hydroquinone/quinone couple fits well the cavity of β-CD.[15] X-ray photoelectron spectroscopy (XPS) and ^{1}H NMR are used to characterize the β-CD/PNAANI film.

2. Experimental Section

2.1. Materials and Procedures. *N*-Acetylaniline and hydroquinone (Shanghai Chemical Works, China) were used after recrystallization from ethanol. β-Cyclodextrin was purchased from Sigma and used without further purification. Other chemicals used were of AR grade. Water was doubly distilled in an all-glass apparatus. All experiments were carried out at room temperature (298 K).

Electrochemical measurements were performed on the LK 98 microcomputer-based electrochemical system (LANLIKE, Tianjin, China). A three-electrode single-compartment cell was used for cyclic voltammetry. A 4 mm diameter glassy carbon electrode (GCE) disk (homemade) was used as the working electrode, a platinum tab as the counter electrode, and a Ag/AgCl electrode as the reference electrode. Before each experiment, a glassy carbon electrode was polished consequently with 1, 0.3, and 0.05 μm α-alumina slurry, rinsed thoroughly with doubly distilled water between each polishing step, sonicated in 1:1 nitric acid, acetone, and doubly distilled water successively, and, then, allowed to dry at room temperature.

The X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using nonmonochromated Mg Kα radiation as the excitation source.

^{1}H NMR experiments on DMSO-d_6 solution were carried out on a Bruker AVANCE 400 NMR spectrometer operated at 400 MHz. Chemical shifts of ^{1}H NMR spectra in DMSO-d_6 at 303 K were referenced to the solvent value (δ = 2.50 ppm).

2.2. Fabrication of Poly(*N*-acetylaniline) (PNAANI) Film Electrode. The PNAANI film electrode was prepared by electrodeposition of PNAANI in a 0.1 M *N*-acetylaniline, 1 M $HClO_4$ solution. The electrolysis was carried out by potential sweeping from −0.2 to 0.9 V for 20 cycles at 100 mV/s. As the electrolysis proceeded, an excellent cohesive brown film was formed on the GCE surface.

2.3. Fabrication of the β-CD Modified PNAANI Electrode. The β-CD modified PNAANI electrode was obtained by electrooxidation of the PNAANI electrode in a 0.05 M β-CD, 0.1 M $LiClO_4$ DMSO solution. The electrooxidation was carried out at a constant potential of 1.2 V for a definite time.

3. Results and Discussion

3.1. Growth of the PNAANI Film. The electrochemical formation of PNANNI film on GCE was performed by multicyclic voltammetry. Figure 1 shows a cyclic voltammogram for the PNAANI film deposition. Three redox couples with $E^{0'}$ about 0.05, 0.45, and 0.65 V are observed. On successive scans, the peak currents increase slightly with each scan. This behavior indicates that a conductive polymeric film is coated onto the electrode.

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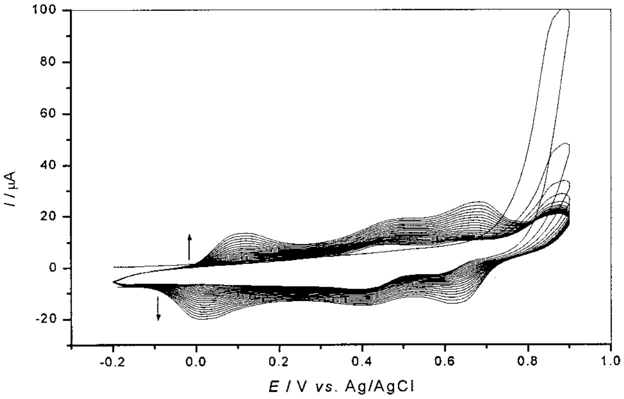


Figure 1. Voltammetric synthesis of PNAANI film from 0.1 M *N*-acetylaniline in 1 M $HClO_4$ on a glassy carbon electrode. Scan rate: 100 mV/s.

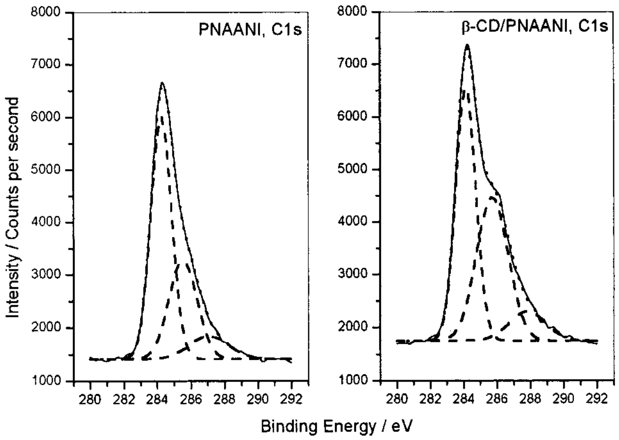


Figure 2. XPS C 1s narrow scans of the PNAANI film and the β-CD/PNAANI film.

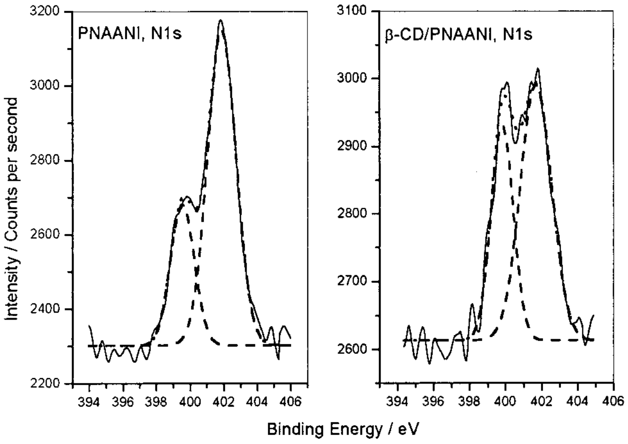
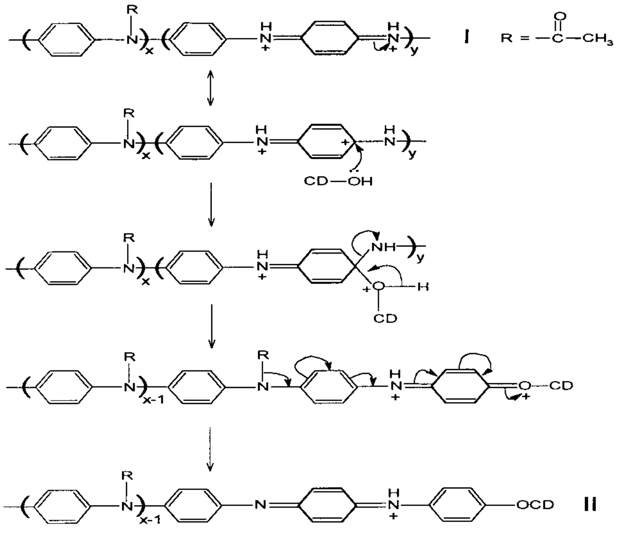


Figure 3. XPS N 1s narrow scans of the PNAANI film and the β-CD/PNAANI film.

Table 1. Comparison of the XPS Peak Areas between the PNAANI Film and β-CD/PNAANI Film

	C 1s			N 1s	
polymer	C−C/C−H	C−N/C−O	C=O	$-\mathrm{N}\langle$	$-\mathrm{NH}^+=$
PNAANI film	7126	3870	1248	718	1468
β-CD/PNAANI film	7500	6048	1727	490	827

Scheme 1. Proposed Mechanism for the β-CD Incorporation into the PNAANI Film



3.2. Characterization of the PNAANI Film and the β-CD/PNAANI Film.

The XPS C 1s and N 1s spectra of the β-CD/PNAANI film are compared with that of the PNAANI film in Figure 2 and Figure 3, respectively. The C 1s XPS signal of PNAANI film can be deconvoluted into three components, C−C or C−H (284.2 eV), C−N or C−O (285.6 eV), and C=O (287.4 eV). The N 1s XPS signal of the PNAANI film can be deconvoluted into two components: the uncharged amine ($-\mathrm{N}\langle$) (399.8 eV) and the generated iminium ions ($-\mathrm{NH}^+=$) (401.8 eV). However, after the PNAANI electrode was electrooxidized in a 0.05 M β-CD, 0.1 M $LiClO_4$ DMSO solution, the peak areas of C−C or C−H (284.2 eV), C−N or C−O (285.6 eV), and C=O (287.4 eV) became larger. The peak areas of ($-\mathrm{N}\langle$) (399.8 eV) and ($-\mathrm{NH}^+=$) (401.8 eV) became smaller. The XPS peak areas of the PNAANI film and β-CD/PNAANI film are compared in Table 1. This can be explained by that the highly oxidized conducting polymer was nucleophilic attacked by the hydroxy group of β-CD. β-Cyclodextrins were attached to the backbone of the polymer, while some of the iminium ions were decomposed. The mechanism can be illustrated in Scheme 1. The structure of PNAANI can be described as I according to the XPS N 1s peaks. The area ratio of ($-\mathrm{N}\langle$) (399.8 eV) to ($-\mathrm{NH}^+=$) (401.8 eV) is 1:2, which means x:y is 1:1. This result is in accordance with Dong and Li.[16,17] They have electropolymerized N-substituted aniline and found that a part of the N-substituted group eliminated from the polymer backbone.

The β-CD/PNAANI film is further studied by ^{1}H NMR. Figure 4 shows the ^{1}H NMR spectra of β-CD and β-CD/PNAANI film in DMSO-d_6. In the ^{1}H NMR spectrum of β-CD/PNAANI, proton signals belonging to the H atoms attached to C1, C2, C3, C4, C5, and C6 of β-CD can be found. However, proton signals belonging to the H atoms attached to O2, O3, and O6 of β-CD disappear. The results can be attributed by that hydroxyl groups of β-CD nucleophilic attack the polymer chain, and the H atoms of hydroxyl groups are lost from β-CD. Furthermore, if β-CD is only absorbed into the PNAANI film, proton signals belonging to the H atoms attached to O2, O3, and O6 of β-CD will remain. Thus, the mechanism for the β-CD incorporation into the PNAANI film (Scheme 1) is further supported by the ^{1}H NMR measurements.

3.3. Effect of β-CD on the Electrochemical Behavior of Hydroquinone.

Cyclic voltammograms of hydroquinone in the absence and presence of β-CD at the PNAANI electrode and β-CD/PNAANI electrode are shown in Figure 5. At the PNAANI electrode, hydro-

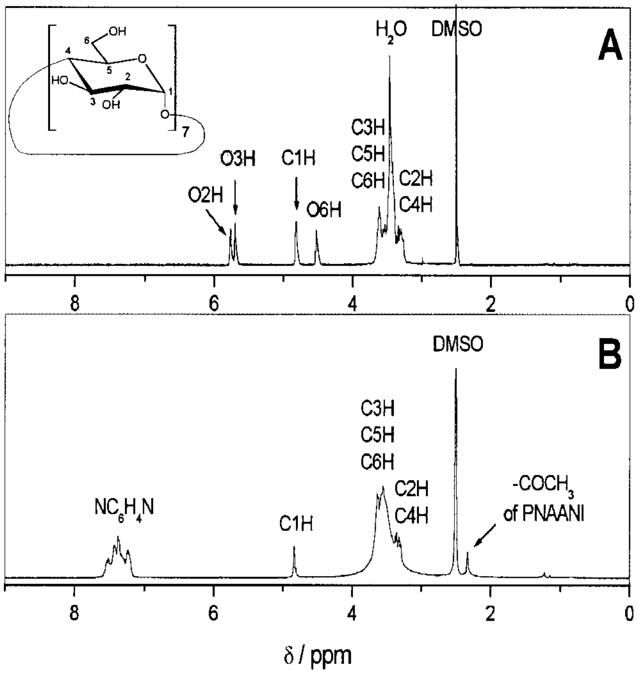


Figure 4. ^{1}H NMR spectra of β-CD (A) and β-CD/PNAANI film (B) in DMSO-d_6.

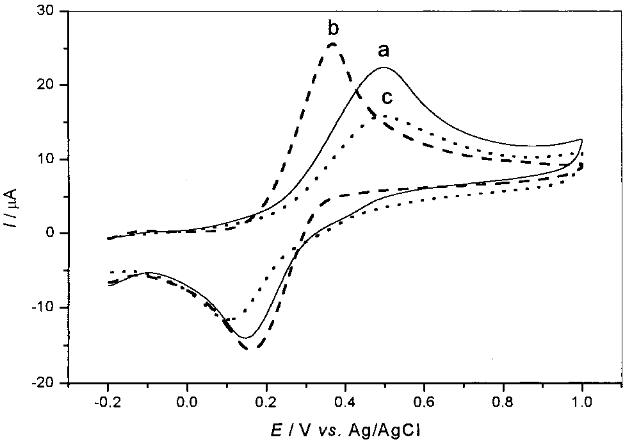


Figure 5. Cyclic voltammograms of 5×10^{-3} M hydroquinone + 0.05 M $NaNO_3$ in 0.05 M phosphate buffer solution (pH 6.8) at the PNAANI electrode (a) and at β-CD/PNAANI electrode (b) and 5×10^{-3} M hydroquinone + 5×10^{-3} M β-CD + 0.05 M $NaNO_3$ in 0.05 M phosphate buffer solution (pH 6.8) at the PNAANI electrode (c). Scan rate: 20 mV/s.

quinone shows a reduction peak at 0.150 V and an oxidation peak at 0.495 V corresponding to the hydroquinone/quinone redox reactions. At the β-CD/PNAANI electrode, the redox peak currents increase, and the reduction peak potential shifts toward a more positive potential of 0.160 while the oxidation peak potential shifts toward a more negative potential of 0.370 V. The ΔE_p of hydroquinone is 210 mV, which is 135 mV sharper than that at the PNAANI electrode. The peak area at the β-CD/PNAANI electrode is 35% larger than that at the PNAANI electrode. The results could be interpreted in the following manner: If the β-CD attached to the polymer backbone acts as an inclusion agent for the hydroquinone, then one expect the peaks to sharpen and shift to a ΔE_p of 0 mV. The observed voltammetric response (line b) is due to hydroquinone molecules included in the cavity of β-CD attached to the PNAANI film and that diffusing hydroquinone molecules in the solution. So ΔE_p of the peaks will be sharper, and the area of the peaks will be larger if more is β-CD is being electrolyzed in the modified film.

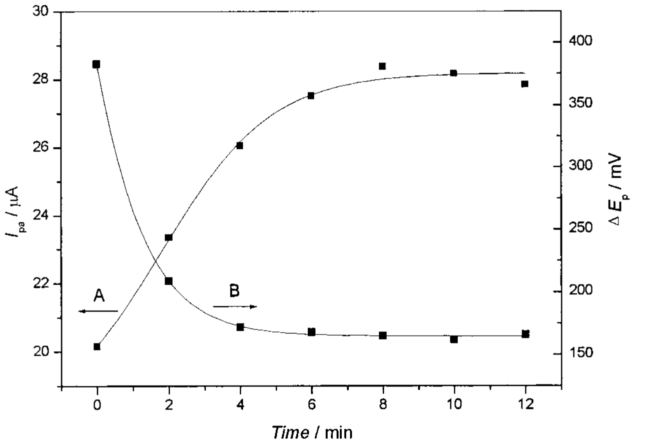
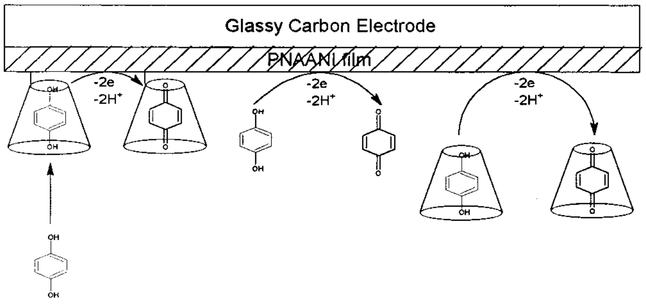


Figure 6. Dependence of I_{pa} (A) and ΔE_p (B) on the time of electrooxidation.

Scheme 2. Schematic Illustration of the β-CD Effect on the Electrochemical Behavior of Hydroquinone



However, after the addition of β-CD to the hydroquinone solution, the redox peak currents of the PNAANI electrode decrease, and the reduction peak potential shifts toward a more negative potential of 0.105 V while the oxidation peak potential remains 0.495 V (almost invariable). The ΔE_p is 390 mV, which is 45 mV wider than that no addition of β-CD. The peak area is 33% smaller than that no addition of β-CD (Figure 5, line c). This is because that β-CD is bulky (1.53 nm) and it can form an inclusion complex with hydroquinone; the hydroquinone–β-CD inclusion complex is more difficult to diffuse to the electrode surface than the hydroquinone molecule. The schematic illustration of the β-CD effect on the electrochemical behavior of hydroquinone is proposed in Scheme 2.

To determine the electrooxidation time when β-CD is incorporated into the PNAANI film saturately, we electrooxidized the PNAANI electrode for various times. A series of cyclic voltammograms of hydroquinone at the β-CD/PNAANI electrodes of various electrooxidation times are performed. The dependence of I_{pa} and ΔE_p on the time of electrooxidation at 1.2 V in 0.05 M β-CD + 0.1 M $LiClO_4$/DMSO is shown in Figure 6. It shows that I_{pa} increases gradually upon increasing the electrooxidation time. An increase in the I_{pa} (36.8%) is observed after 6 min of electrooxidation. Further increase of the electrooxidation time did not show any effect on the cyclic voltammogram. ΔE_p decreases gradually with increase of the electrooxidation time, and finally, it reaches a limiting value after 6 min of electrooxidation. This observation shows that β-CD incorporated at the PNAANI film is saturated after 6 min of electrooxidation.

The stability of the β-CD modified PNAANI electrode was examined by measuring the I_{pa} response of hydroquinone after various successive sweeping cycles. The activity of the electrode remained at 90.9% of the original value after 500 cycles.

4. Conclusion

It has been shown that β-CD can be easily incorporated into the PNAANI film in the DMSO solution at a potential of 1.2 V. XPS spectra and ^{1}H NMR spectra show that β-CD is attached to the backbone of PNAANI film. In the cyclic voltammogram of hydroquinone at the β-CD/PNAANI electrode, ΔE_p of the peaks is sharpening and the area of the peaks is increasing, which can be due to the inclusion of hydroquinone into the cavity of β-CD immobilized at the electrode surface.

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