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Crystalline polythiophene film prepared by electrochemical polymerization of thiophene at a nickel electrode

Chun Li[a], Gaoquan Shi[a,*], Yingqiu Liang[a] and Zhaolin Sha[a]
[a]Department of Chemistry and National Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China
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Crystalline polythiophene (Pth) film was first electrochemically deposited onto a nickel substrate from freshly distilled BF_3-diethyl ether (BFEE) solution containing 15 mM thiophene. The crystalline film was studied by the X-ray diffraction technique and it was found to be a monoclinic unit cell with parameters $a = 0.624$ nm, $b = 0.593$ nm, $c = 0.596$ nm, and $\beta = 103.6°$. The film obtained from this medium has a compact morphology and great strength. © 1997 Elsevier Science Ltd.

(Keywords: polythiophene; electropolymerization; crystalline)

Introduction

Much work has already been devoted to the electrochemical synthesis and study of polythiophene film (Pth), mainly due to its having many advantages over polypyrroles and other organic electrically conducting materials[1,2]. Pth has been successfully deposited on noble metals (Pt, Au) at relatively high applied potentials. However, there have been few studies concerned with the electrochemical polymerization of thiophene on oxidizable metals[3,4].

Although the Pths chemically synthesized by Grignard coupling of 2,5 diiodothiophene have partial crystallinity[5], it is believed that the Pths obtained via the electrochemical routes are rather non-crystalline materials with a broad amorphous halo in the wide-angle X-ray diffraction region, and with a weak small-angle peak corresponding to a periodic structure from the planar configuration of the polymer backbone[6–8].

Recently, we found Pth films could be deposited onto a nickel electrode at low potential (about 1.2 V versus Ag/AgCl) in freshly distilled BFEE solution. The obtained film was shiny and flexible, and surprisingly we found that the film had high crystallinity. Here, we report the preliminary results.

Experimental

Conductive Pth synthesis and electrochemical examinations were performed in a one-compartment cell using a computer-controlled EG&G potentiostat, model 273 (Princeton Applied Research Co.). The working and counter electrodes were nickel sheets (3 × 3 cm) placed 0.5 cm apart. Ag/AgCl was the reference electrode (AgCl coated Ag directly in solution). To provide a more general reference, we examined the ferrocene–ferrocenium redox couple in freshly distilled BFEE, and its half-wave potential $[1/2(E_{p,a} + E_{p,c})$, where a = anodic and c = cathodic] was found to be 0.331 V (versus Ag/AgCl). Thus a correction of 0.069 V (−0.331 + 0.400 V) was needed to bring the measured potentials in BFEE originally versus Ag/AgCl to potentials versus the standard hydrogen electrode[9]. The electrolyte used for the Pth deposition was freshly distilled BFEE (no other solvent and supporting salt were added) containing 15 mM thiophene. BFEE may exist in diethyl ether as a polar molecule[10], $(C_2H_5)_3O^+$, BF_4^-, which supports the conducting medium (dopant). All solutions were deareated by a dry argon stream and maintained at a slight over-pressure during the experiments. The integrated charge passed during film growth was used to control the thickness of the deposited films. As-grown films were well washed with distilled methanol and ethyl ether, and then dried under vacuum at 80°C for 24 h before characterization was carried out. The film thicknesses were determined with the 'Heiderham' thickness monitor. The tensile strength of the film was measured by using an electronic stretching machine (WD1, Changchun). dc conductivity was measured by the conventional four-probe electrode technique. X-ray diffraction examination was carried out by using a wide-angle X-ray diffractometer (Shimadzu, XD-3A) with a Cu target. The transmission infrared spectrum of the Pth film was recorded from a KBr pellet on a Nicolet 170 SX FT-IR spectrometer.

Results and discussion

The deposition of Pth onto a Nickel substrate can be detected by cyclic voltammograms of thiophene in BFEE solution as shown in *Figure 1*A. On the first cycle, the cathodic excursion of the potential gives a voltammogram with more anodic current densities (in the +1.4 to +1.0 V region) than the obtained for anodic excursion. The formation of this loop is characteristic of the nucleation processes, as reported in the literature[1], and only appears on the first voltammogram. At the same time, the potential scans shown led to the formation of a film on the electrode surface (purple to black as the deposit thickened). The strong oxidation present at potentials greater than 1.0 V, which promoted polymer generation on the electrode, can be observed on the voltammogram. The polymer was reduced and oxidized between 0.4 and 0.6 V. The increase of the redox wave current implied that the amount of the polymer on the electrode increased. The potential shift of this maximum provided information about the increases of the electrical resistance in the polymer film and the over-potential needed to overcome that resistance[11,12]. The CV of freshly distilled BFEE solution showed no current

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[*] To whom correspondence should be addressed.

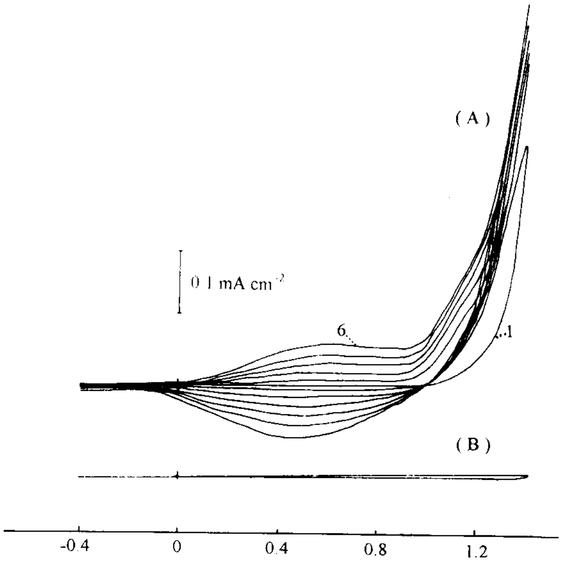

Figure 1 Cyclic voltammograms of 15 mM thiophene in freshly distilled BFEE (A), or pure BFEE (B) at a nickel electrode and a potential scan rate of 100 mV/s. The numbers indicate successive potential cycles.

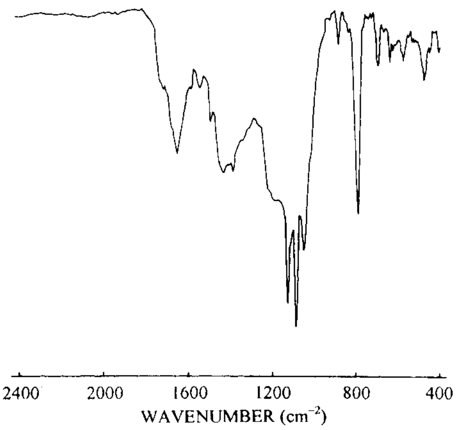

Figure 2 Transmission infrared spectrum of Pth film obtained at a current density of 0.5 mA cm^{-2}.

waves in the same potential scale (*Figure 1*B), which demonstrated that the electrolyte and the electrode were electrochemically inert during film growth.

The Pth film obtained from the BFEE medium and at a steady electrolysis current density of 0.5 mA cm^{-2} was very shiny and flexible. The conductivity of this film, measured by the conventional four probe electrode technique, was 3.5×10^{-2} S cm^{-1}. The tensile strength of this film was measured to be 800 ± 50 kg cm^{-2} at a stretching rate of 5 cm min^{-1}. This value is much higher than those for the Pth films obtained from other media[13,14].

The transmission infrared spectrum (*Figure 2*) of the Pth film prepared at 0.5 mA cm^{-2} showed aromatic stretching bands at 1491, 1436 and 1321 cm^{-1}. Two very strong bands attributed to the C–C vibration and C–H deformation were found at 1122 and 1083 cm^{-1}, respectively. A very strong absorption at 788 cm^{-1} was assigned to the C–H out of plane vibration of the 2,5-disubstituted thiophene ring (due to α,α' polymerization). The band at 701 cm^{-1} ascribed to the C–H out of plane vibration of the monosubstituted thiophene ring is very weak, which indicates that the degree of polymerization of the obtained Pth is very high[3]. The C–S stretching vibration band appeared at 636 cm^{-1}.

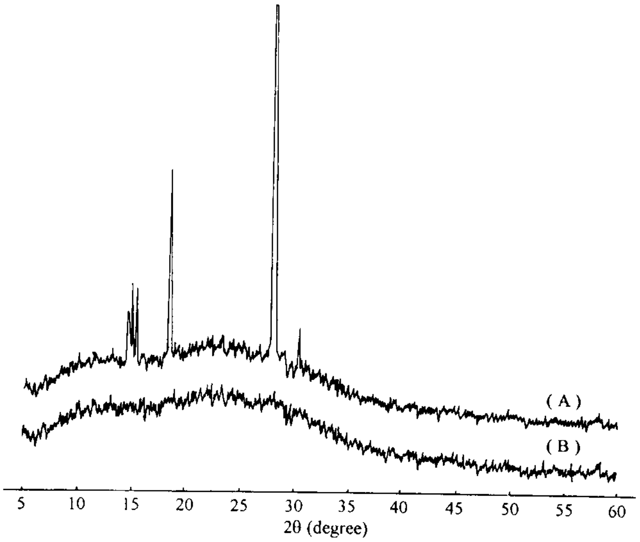

Figure 3 Wide-angle diffraction patterns of 1 μm Pth film (same as Fig. 2) coated on a glass substrate (A) and naked glass substrate (B).

*Figure 3*A illustrates the wide-angle X-ray diffraction pattern recorded from the Pth film (coated on a glass substrate) with a thickness of ≈ 1 μm. As can be seen from this figure, a series of sharp Bragg diffraction peaks were found in the range $10 < 2\theta < 30°$. We have indexed the reflections using a monoclinic unit cell with parameters $a = 0.624$, $b = 0.593$, $c = 0.596$ and $\beta = 103.6°$. *Figure 3*B shows the diffraction pattern of the glass substrate. When comparing *Figure 3*A and *Figure 3*B, it is reasonable to conclude that the weak diffuse scattering background shown in *Figure 3*A is mainly attributable to that of the glass substrate and the Pth film has a high crystallinity, of over 70%.

In conclusion, the Pth film deposited on the nickel electrode from the electrolyte of the BFEE solution containing 15 mM thiophene has a high mechanical strength and a high crystallinity.

Acknowledgements

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