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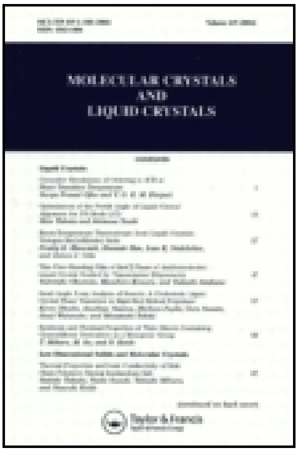

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Magnetic Field Effects on Photoelectrochemical Reactions of Electrodes Modified with Poly(3-hexylthiophene) Nanowires

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Magnetic Field Effects on Photoelectrochemical Reactions of Electrodes Modified with Poly(3-hexylthiophene) Nanowires

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Magnetic field effects (MFEs) on photoelectrochemical reaction of electrodes modified with nanowires consisting of regioregular poly(3-hexylthiophene) (P3HT) and disordered P3HT films without and with anneal treatments were examined. The MFEs on the photocurrents were observed in three modified electrodes. The magnitude of the MFEs increased with the following order of modified electrodes: P3HT nanowires, P3HT films with anneal treatment, and P3HT films without anneal treatment. The difference of the MFEs is most likely attributable to the facility of hole hopping between the adjacent thiophenes in the P3HT structures.

Keywords Hole hopping; magnetic field effect; nanowire; photoelectrochemical reaction; polythiophene; radical pair mechanism

Introduction

Nanowires of regioregular poly (3-alkylthiophene) have been prepared by whisker precipitation in a solution [1–5]. The nanowires have also been finding use as promising materials for optoelectronic applications.

Recently, we reported that the photocurrent of the electrode modified with poly(3-hexylthiophene) (P3HT) nanowires was approximately twice as large as that from the electrode modified with disordered P3HT films and this is most likely because hole hopping between adjacent thiophenes is facilitated in the P3HT nanowires due to π-π stacking [5]. The mechanisms of photochemical reactions in the condensed phase have been explained by invoking magnetic field effects (MFEs) on reaction kinetics or yields [6]. Previously, we examined the MFEs on the photoelectrochemical reactions of photosensitive modified electrodes [7–11]. However, the MFEs on the photoelectrochemical reactions of the P3HT nanowires have not yet been examined. In this study, we examined the MFEs on the photoelectrochemical reactions of electrodes modified with nanowires consisting of P3HT

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and disordered P3HT films without and with anneal treatments to verify the mechanisms of the photoelectrochemical reactions of electrodes modified with P3HT nanowires.

Experimental

Regioregular P3HT (Aldrich) (7 or 12.5 mg) was dissolved in anisole or chlorobenzene (0.5 ml). The P3HT nanowires were obtained using an anisole solution of P3HT cooled from 353 K to room temperature [2–5]. The anisole and chlorobenzene solutions of P3HT (50 μl) were spin-coated onto on a mica or an indium tin oxide (ITO)-electrode (10 Ω/sq.). Two samples using chlorobenzene solutions of P3HT were prepared with and without anneal treatments (423 K, 10 min.). The sample using the anisole solution of P3HT was prepared without anneal treatment. Absorption spectra (Shimadzu UV-3150), scanning electron microscope (SEM) (Hitachi High-Tech SU8000), and photoelectrochemical measurements of the sample on the ITO-electrodes modified with the P3HT nanowires and the disordered P3HT films with anneal treatment were carried out. Wide-angle X-ray diffraction patterns were obtained on a XRD instrument (Rigaku, Smart Lab, $\lambda = 1.54056$Å (Cu/Kα1)) [3].

The photoelectrochemical measurements of three modified electrodes were carried out by using a three electrode cell in the presence of methylviologen (MV^{2+}) (20 mM) and O_2 as an electron acceptor under ambient atmosphere as similar to the previous papers [7–11]. The MFEs on the photocurrent were measured as similar to our previous papers [7–11]. The electric field was applied parallel to the magnetic field to avoid perturbations due to the magneto-hydrodynamic force [7].

Results and Discussion

Characterization of Electrodes Modified with P3HT Nanowires and P3HT Films with and without Anneal Treatments

A number of P3HT nanowires were observed in the SEM image of the ITO electrode prepared from P3HT anisole solution (Fig. 1(a)) as reported in the previous papers [10, 11]. In contrast, the P3HT nanowires were hardly observed in SEM image of the ITO-electrode with or without anneal treatment prepared from P3HT chlorobenzene solution (Fig. 1(b)).

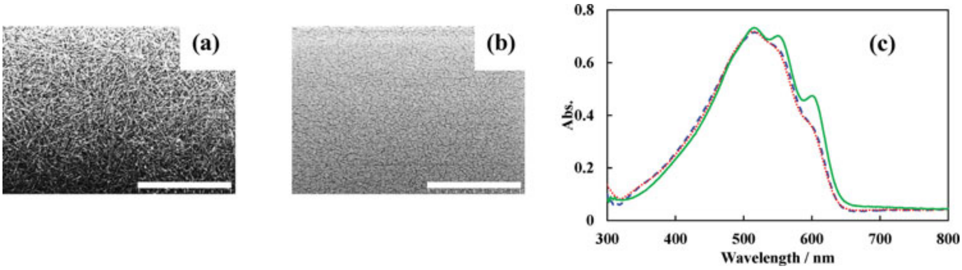

Figure 1. SEM images of (a) the modified ITO-electrode prepared from P3HT anisole solution and (b) the modified ITO-electrode with anneal treatment prepared from P3HT chlorobenzene solution (scale bar = 1 μm). (c) Absorption spectrum of P3HT nanowires that was prepared from anisole (green solid line), and absorption spectra of P3HT films with (red dotted line) and without anneal treatment (blue broken line) that were prepared from the chlorobenzene solution of P3HT nanowires on ITO electrodes.

Three absorption bands (515, 551, and 600 nm) in the P3HT nanowires prepared from anisole solution (Fig. 1(c)) indicate the formation of the structures composed of highly ordered polymer chains [2–5]. In contrast, these bands were hardly observed in the P3HT films prepared from chlorobenzene solution (Fig. 1(c)). These results of the absorption spectra are in good agreement with those of the SEM images (Fig. 1).

The XRD patterns of the P3HT nanowires and two P3HT films with and without anneal treatments on the ITO-electrodes were measured. The reflection peaks from (100) were observed (d-spacing 16.2 Å for P3HT nanowires, 16.8 Å for P3HT films with anneal treatment, and 16.9 Å for P3HT films without anneal treatment). The half peak width increased with the following order of modified electrodes: P3HT nanowires, P3HT films with anneal treatment, and P3HT films without anneal treatment. From these XRD results, the magnitude of the formation of the P3HT nanostructures with a lamellar organization of the polymer chains with π-π stacking of thiophenes become larger with the following order of modified electrodes: P3HT films without anneal treatment, P3HT films with anneal treatment, and P3HT nanowires [2–5].

MFEs on the Photocurrents of Electrodes Modified with P3HT Nanowires and P3HT Films with and without Anneal Treatments

Photoirradiation of visible light ($\geq$ 400 nm) upon three modified electrodes afforded stable cathodic photocurrents at -0.1 V vs Ag/AgCl in the presence of MV^{2+} and O_2. Therefore, the photocurrents of these modified electrodes were ascribed to photoinduced electron-transfer reaction from excited state of P3HT to MV^{2+} and O_2 in bulk aqueous solution.

We examined the MFEs on the photoelectrochemical reactions of three modified electrodes. The photocurrent increased in the presence of magnetic field. The magnitude of MFEs on the photocurrent is expressed as

$$Q = (I(B) - I(0))/I(0) \times 100, \tag{1}$$

where I(0) and I(B) are the photocurrent in the absence and presence of the magnetic field (B), respectively, as reported in the previous papers [7–11]. In the electrode modified with P3HT nanowires, the Q value (%) increased gradually with magnetic field. On the other hand, in the P3HT films with and without anneal treatment, the Q values (%) increased steeply for lower magnetic fields ($B \leq 10$ mT) and increased gradually for higher magnetic fields ($B \geq 10$ mT) (Fig. 2). These MFEs (Fig. 2) were similar to those in the modified electrodes in the previous papers [7, 9–11]. Therefore, the MFEs in the lower fields and the higher fields are probably explained by hyperfine coupling and relaxation mechanisms in radical pair (electron-hole pair) mechanism, respectively [6–12]. Interestingly, the MFEs due to hyperfine coupling mechanism disappeared in the electrode modified with P3HT nanowires [13,14]. The magnitude of MFEs in the electrode modified with P3HT nanowires was much smaller than those in the electrode modified with P3HT with and without anneal treatments. The results are probably attributable to the fast hole hopping in the P3HT nanowires, as described below.

The magnitude of MFEs increased with the following order of modified electrodes: P3HT nanowires, P3HT films with anneal treatment, and P3HT films without anneal treatment (Fig. 2). Therefore, the difference of the MFEs is most likely ascribed to the ordered nanostructures of P3HT in three electrodes and the magnitude of the MFEs probably becomes smaller with being ordered structures. In other words, the difference is most likely attributable to the facility of hole hopping between the adjacent thiophenes in the P3HT

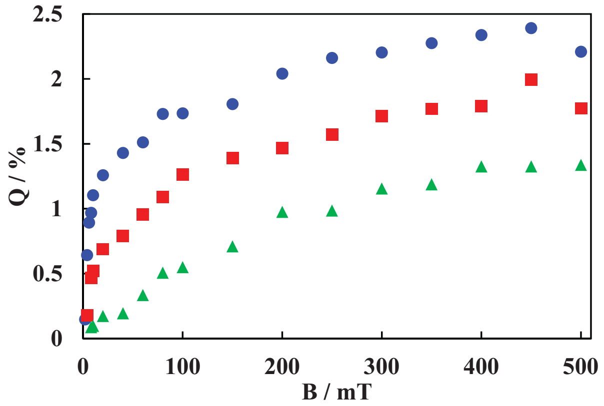

Figure 2. Magnetic field dependence of the Q values of the electrodes modified with P3HT nanowires (▲) and P3HT films with anneal treatment (■) and without anneal treatment (●).

structures [5]. Further investigations on the mechanism of the MFEs on photoelectrochemical reactions using the P3HT nanowires are now in progress.

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