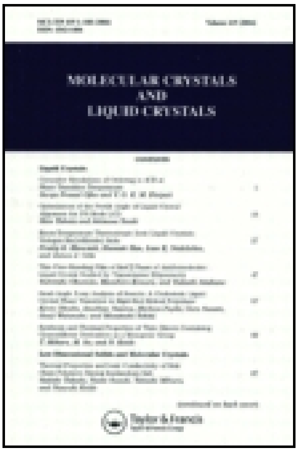

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Photoelectrochemical Reactions of Electrodes Modified with Poly(3-hexylthiophene) Nanowires

Hiroaki Yonemura [a], Koichi Yuno [b], Masayuki Takata [c] & Sunao Yamada [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Motooka, Nishi-ku, Fukuoka, Japan

[b] Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Motooka, Nishi-ku, Fukuoka, Japan

[c] Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Motooka, Nishi-ku, Fukuoka, Japan

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Photoelectrochemical Reactions of Electrodes Modified with Poly(3-hexylthiophene) Nanowires

HIROAKI YONEMURA,[1] KOICHI YUNO,[2]
MASAYUKI TAKATA,[3] AND SUNAO YAMADA[1]

[1]Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Motooka, Nishi-ku, Fukuoka, Japan
[2]Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Motooka, Nishi-ku, Fukuoka, Japan
[3]Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Motooka, Nishi-ku, Fukuoka, Japan

Nanowires consisting of regioregular poly(3-hexylthiophene) (P3HT) were prepared by whisker precipitation from a solution of P3HT in anisole. Photoirradiation of two electrodes modified with P3HT nanowires or P3HT with visible light afforded cathodic photocurrents in the presence of O_2*. The photocurrent of the electrode modified with P3HT nanowires was approximately twice as large as that from the electrode modified with P3HT. This is most likely because hole hopping between adjacent thiophenes is facilitated in the P3HT nanowires due to* π-π *stacking.*

Keywords Hole hopping; nanowire; photoelectrochemical reaction; polythiophene; π-π stacking

Introduction

Conducting polymers with π-conjugated electronic structures have been widely used in optoelectronic devices such as light emitting diodes, photovoltaic cells and field effect transistors [1–3]. Nanowires of regioregular poly(3-alkylthiophene), which are prepared by precipitation from solution [4–9], are materials for optoelectronic applications.

The fabrication of high performance nanowires is enabled by the ability to exploit anisotropic orientation to obtain structures with desired properties. Recently, we reported that nanowires consisting of regioregular poly(3-hexylthiophene) (P3HT) or poly(3-butylthiophene) partly oriented their long axes parallel or perpendicular to the π-π stacking direction, being perpendicular or parallel to the magnetic field [8,9]. In this study, we modified electrodes with P3HT nanowires or disordered P3HT and investigated the effect of P3HT structure on the photoelectrochemical reactions of the modified electrodes.

Address correspondence to Hiroaki Yonemura, Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. E-mail: yonemura@mail.cstm.kyushu-u.ac.jp

Experimental

P3HT (Mw = 30,000∼87,000) was purchased from Aldrich. Anisole (Wako guaranteed reagent) was used as received. P3HT nanowires were prepared using anisole similar to methods reported previously [4–9]. P3HT (1 mg) was dissolved in anisole (2 mL). P3HT nanowires were obtained by cooling the solution from 353 K to room temperature. As a reference, an unheated solution of P3HT in anisole was also prepared at room temperature.

Using a syringe, 6 µL of a solution of P3HT in anisole that was heat treated or unheated was dropped on a mica or an indium tin oxide (ITO) electrode (Surface Resistivity: 10 Ω/sq.). After drying to remove the solvent, atomic force microscope (AFM) measurements of the samples on mica and photoelectrochemical measurements of the modified electrodes were carried out. AFM images were recorded in tapping mode using a Nanoscope IIIa (Digital Instrument). Absorption spectra of the solutions were recorded on a Shimadzu UV-3150 spectrometer at room temperature [8,9]. Wide-angle X-ray diffraction (XRD) patterns were obtained on a diffractometer (Rigaku MultiFlex, (Cu/Kα 1)) [8].

Photoelectrochemical measurements were performed using a three electrode cell containing a P3HT-modified electrode as the working electrode, a platinum electrode as the counter electrode, and a Ag/AgCl electrode as the reference electrode as described in previous papers [10,11]. Measurements were obtained under O_2 atmosphere by bubbling O_2 through the electrolyte for 30 min. Na_2SO_4 (0.1 M) was used as the supporting electrolyte.

Results and Discussion

Characterization of P3HT Nanowires

Figure 1(a) shows that there a number of P3HT nanowires were formed in the solution of P3HT in anisole that was heat treated. The AFM images (Figs. 1(a) and 1(c)) indicate the nanowires are longer than 5 µm, are 3–10 nm in height, and have widths of 100–120 nm. In contrast, few P3HT nanowires formed when the solution of P3HT in anisole was not heated in AFM image (Fig. 1(b)). The absorption spectra of the heat-treated and unheated P3HT solutions differ from each other (Fig. 2), also suggesting that heat treatment is required for the formation of nanowires. XRD analysis of a P3HT film cast from anisole solution that was heat treated further confirmed the formation of P3HT nanowires, with a lamellar organization of the polymer chains with π-π stacking in the direction of the nanowires [4–9].

Photoelectrochemical Reactions of Electrodes Modified with P3HT Nanowires or P3HT

Photoirradiation of the electrode modified with P3HT nanowires with visible light (≥400 nm) afforded stable cathodic photocurrents at 0 V *vs.* Ag/AgCl in the presence of O_2 as an electron acceptor in aqueous solution (Fig. 2). A peak was observed at 520 nm in the photocurrent action spectrum. The action spectrum of the electrode modified with P3HT nanowires (≥470 nm) agrees closely with the absorption spectrum of the P3HT nanowires in anisole. The bands as peaks or shoulders at 500, 520, 550, and 600 nm in the photocurrent action spectrum strongly indicate that

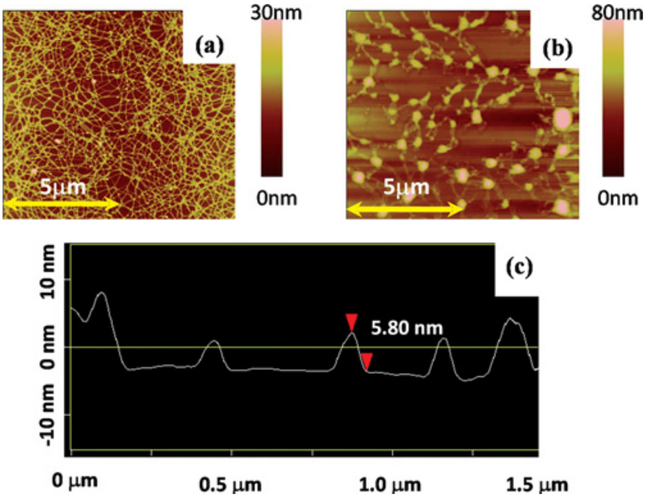

Figure 1. (a) AFM image of P3HT nanowires cast on mica that were grown from a solution of P3HT that were heat treated. (b) AFM image of P3HT cast on mica that were grown from a solution of P3HT that were not heated. (c) Cross-sectional view of the P3HT nanowires in AFM image (a).

the photocurrents are mainly attributable to excitation of the P3HT nanowires as reported in the previous paper [12].

Cathodic photocurrents were also observed from the electrode modified with P3HT. A broad photocurrent action spectrum was observed with a peak at 510 nm a shoulder at 600 nm. The photocurrent action spectrum was blue-shifted compared with that for the P3HT nanowires, and the spectral features were different. In the AFM image (Fig. 1(b)) with unheated treatment, the P3HT nanowires were

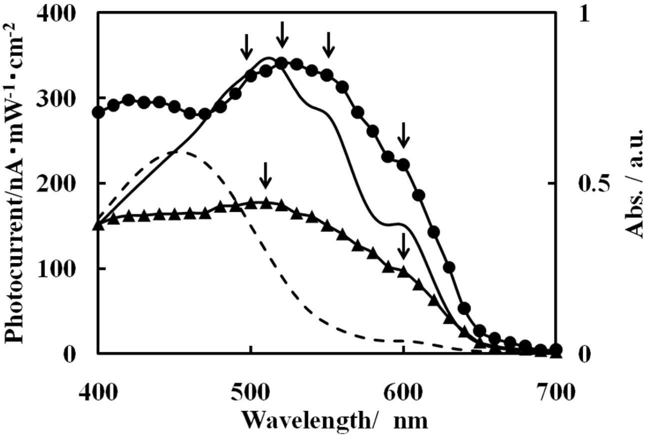

Figure 2. Photocurrent action spectra of ITO electrodes modified with P3HT nanowires (●) or P3HT (▲), and absorption spectra of solutions of P3HT in anisole that were heat treated to form P3HT nanowires (solid line) and unheated (disordered P3HT) (broken line). The peaks and the shoulders in two photocurrent action spectra were shown as arrows (↓).

hardly observed. On the basis of the photocurrent action spectrum and the AFM image indicate that the photocurrent from the electrode modified with P3HT arose from disordered P3HT, not P3HT nanowires.

The photocurrent from the electrode modified with P3HT nanowires was about twice that from the electrode modified with P3HT, which is ascribed to the formation of P3HT nanowires. The enhanced photocurrent is most likely caused by the P3HT nanowires facilitating hole hopping between adjacent thiophenes involved in π-π stacking.

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