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Alternate network film of thiol group-terminated polythiophene and gold nanoparticle

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Abstract

The thiol group-terminated polythiophenes were prepared via the Pd-catalyzed coupling reaction of the bromo group-terminated polythiophene derivatives and methylthiophenylboronic acid, and were mixed with the nanometer-sized gold particle to form a self-assembled network film of the alternate conjugation of the polythiophene with the gold nanoparticle. The electron microscopy and X-ray photoelectron spectroscopy of the films supported the formation of a polythiophene/gold nanoparticle alternate network structure through the S–Au linkages. The high electric conductivity and its low activation energy on the network film suggested that the conductive characteristic of the film originated from that of the π-conjugated polythiophene backbone connected with the gold nanoparticle.

Keywords: Polythiophene; Gold nanoparticle; Self-assembly

1. Introduction

The combination of π-conjugated organic polymers and nanometer-sized metal particles has attracted considerable attention because of its potential applications for catalysts, sensors, batteries, light-emitting diodes, and photovoltaic cells [1–3]. The combination or connection of the conjugated polymers with the metal nanoparticles has been achieved by various procedures, such as molecular self-assembly, sol–gel synthesis, and electrochemical deposition to form colloids, films, and bulk materials [4–8]. They often showed characteristic electrical, optical, and mechanical properties. For example, the combination of polythiophene and gold nanoparticle showed electric conductivity enhancement in comparison with the same polymer without the nanoparticle [9]: it was described that the homogeneously dispersed gold nanoparticle in the polythiophene film acted as a conductive pathway among the π-conjugated polythiophenes. In order to take full advantage of the properties of the π-conjugated polymers and metal nanoparticles, a new approach by connecting the π-conjugated polymer backbone and the metal nanoparticle with a conjugated linkage is crucial.

We report in this paper, for the first time, the preparation and conductive characteristic of the polythiophene/gold nanoparticle alternate network film by using the thiol group-terminated polythiophenes, where the π-conjugated polythiophene backbone is connected with gold nanoparticles through the S–Au bonds to form a three-dimensional conjugated network structure. We selected polythiophene and gold nanoparticle as the conjugated polymer and the metal nanoparticle because the electrical and optical properties and the various applications of both have been widely studied [10–12]. The thiol group-terminated poly(3-hexylthiophene-2,5-diyl) **1** was synthesized by the coupling reaction of the corresponding bromo group-terminated polythiophene with 4-(methylthio)phenylboronic acid (Chart 1). Compound **1** was mixed with the gold nanoparticle to form a self-assembled alternate network film of the thiol group-terminated polythiophene and the gold nanoparticle through the conjugated

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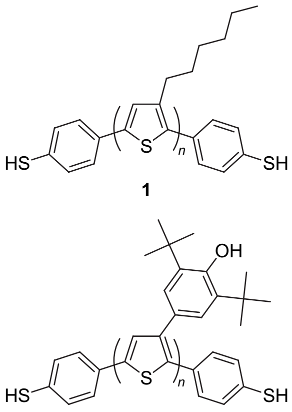

1

2

Chart 1.

S−Au bond linkage. Another polythiophene/gold nanoparticle network film was prepared similarly using the thiol group-terminated poly[3-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)thiophene-2,5-diyl] **2** [13,14], in which the pendant 2,6-di-*tert*-butylphenol group has the potential for generating a phenoxyl radical to display a ferromagnetic spin alignment of the radical's unpaired electrons through the π-conjugated backbone [13,15,16]. The morphology and conductive characteristics of the polythiophene/gold nanoparticle network films are described.

2. Experimental

2.1. Polymerization

Monomers, 2,5-dibromo-3-hexylthiophene **3a** and 2,5-dibromo-3-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)thiophene **3b**, were synthesized based on our previous study [13,14]. To a DMF solution (8 ml) of the monomer **3b** (0.976 g, 2.0 mmol) were added 0.25 ml of 1,5-cyclooctadiene (2.0 mmol), 2,2′-bipyridine (0.375 g, 2.4 mmol), and $Ni(cod)_2$ (0.660 g, 2.4 mmol). The mixture was stirred at 95 °C for 72 h under an N_2 atmosphere, and was poured into HCl-acidic methanol to yield a yellow precipitate, which was washed with diluted HCl, methanol, and an aqueous solution of disodium ethylenediamine tetraacetate. The precipitate was dissolved in CH_2Cl_2 and poured into methanol to give the purified polymer, poly[3-(3′,5′-di-*tert*-butyl-4′-acetoxyphenyl)thiophene-2,5-diyl] α,ω-dibromide (**4b**): yield 0.57 g (58%). IR (KBr pellet, cm^{-1}): 2961 (ν_{C-H}), 1764 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$, 500 MHz, ppm): $\delta = 7.43-7.29$ (br, 2H, phenyl), 7.25 (br, 1H, thiophene), 2.31 (s, 3H, $-OCOCH_3$), 1.37−1.19 (br, 18H, *t*-butyl). The number-average molecular weight (M_n) and polydispersity (M_w/M_n) were determined to be 4500 (degree of polymerization = 13.2) and 1.1, respectively, by gel permeation chromatography (GPC) with polystyrene calibration. Compound **3a** was similarly polymerized to yield poly(3-hexylthiophene-2,5-diyl) α,ω-dibromide **4a** ($M_n = 2400$, $M_w/M_n = 1.7$, degree of polymerization = 13.4).

2.2. Terminal group introduction

Tetrakis(triphenylphosphine) palladium (3.7 mg, 0.0032 mmol) and an aqueous sodium carbonate (0.045 g, 0.428 mmol) solution (0.07 ml) were added to a distilled THF solution (0.86 ml) of the bromo group-terminated polythiophene **4b** (0.240 g, $[-Br] = 0.107$ mmol) and 4-(methylthio)phenylboronic acid (0.161 g, 1.07 mmol). The resulting solution was refluxed for 48 h under an N_2 atmosphere. The polymer was purified by reprecipitating twice from the CH_2Cl_2 solution into methanol to give an orange powder **5b**: yield 0.15 g (64%). IR (KBr pellet, cm^{-1}): 2964 (ν_{C-H}), 1763 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$, 500 MHz, ppm): $\delta = 7.43-7.31$ (br, 2H, phenyl), 7.29 (d, 0.10H, phenyl), 7.25 (d, 0.10H, phenyl), 7.16 (br, 1H, thiophene), 2.46 (s, 0.21H, SCH_3), 2.33 (s, 3H, $-OCOCH_3$), 1.37−1.22 (br, 18H, *t*-butyl). Then, to a distilled *N*,*N*-dimethylacetamide (6.1 ml) solution of **5b** (100 mg, $[-SCH_3] = 0.042$ mmol), grains of ground sodium (0.0145 g, 0.625 mmol) were carefully added at −40 °C under an N_2 atmosphere. After stirring the solution at 110 °C for 72 h, the solution was poured into a 1 M HCl/methanol (1/1) solution. The precipitate was filtrated and washed with methanol to yield **2**: yield 0.089 g (89%). IR (KBr pellet, cm^{-1}): 3638 (ν_{O-H}), 2917 (ν_{C-H}). ^1H NMR ($CDCl_3$, 500 MHz, ppm): $\delta = 7.25$ (d, 0.10H, phenyl), 7.22 (d, 0.10H, phenyl), 7.12−7.17 (br, 3H, thiophene, phenyl), 5.31 (s, 1H, −OH), 0.92−1.68 (br, 18H, *t*-butyl). The hexyl-substituted polythiophenes, **5a** and **1**, were obtained by a similar procedure.

2.3. Formation of the polythiophene/gold nanoparticle alternate network film

The gold nanoparticle stabilized with tetraoctylammonium bromide **AuNP** was prepared according to a previously reported method [12]. The comb-shaped gold electrodes with micrometer gaps [14] were immersed into a 4.0 wt% toluene solution (10 ml) of **1** for 30 min, and then a 0.4 wt% toluene suspension (10 ml) of **AuNP** was added. The mixture was kept standing for 72 h at room temperature under an N_2 atmosphere. The insoluble film on the electrode was washed with toluene using an ultrasonic cleaner to remove excess compounds, and dried in vacuum at 50 °C for 3 h. Other films on electrodes were similarly prepared.

2.4. Measurements

The electric conductivity of the samples on the micro comb-shaped electrodes was measured in the temperature range of 200−275 K by a Keithley 6517A sourcemeter and a Quantum Design MPMS-7 cryostat. The ^1H and ^{13}C NMR, mass, IR, UV−vis, fluorescence, and XPS spectroscopies were performed using a JEOL Lambda 500, a Shimadzu GCMS-QP5050, a JASCO FT/IR-410, a JASCO V-500, a Hitachi F-4500, and a JASCO JPS-9010TR, respectively. The GPC, TGA, FE-SEM, and TEM analysis were carried out using a TOSOH HLC-8220, a Rigaku TG8120, a Hitachi S-4500S, and a JEOL JEM-1011, respectively.

3. Results and discussion

The thiol group-terminated polythiophenes, **1** and **2**, were synthesized as shown in Scheme 1. The UV–vis absorption and fluorescent spectra of the precursor polythiophenes, **4a** and **4b** (degree of polymerization = 13.4 and 13.2, respectively), in a dichloromethane solution gave the absorption maxima (λ_{max}) and fluorescent maxima (λ_{em}) at 398 and 538 nm for **4a** and at 398 and 534 nm for **4b**, respectively, suggesting an extended π-conjugation in the polythiophene backbone.

Methylthiobenzene was introduced as the terminal groups of the polythiophene backbone by the Pd-catalyzed coupling reaction between the terminal bromo groups of the polythiophenes, **4a** and **4b**, and an excess amount of 4-(methylthio)-phenylboronic acid. As the protection group for the thiol group, a methyl group was appropriate for the Pd-catalyzed coupling reaction under the basic condition, whereas the acetyl or alkylsilyl groups were inadequate for the reaction due to the deprotection reaction and the following deactivation of the Pd catalyst with the generated thiol group. The introduction ratio of 4-(methylthio)phenylboronic acid into both terminals of the polythiophene backbone was estimated to be ca. 200% based on the signal ratio of the ^{1}H NMR, that is, the polythiophene possesses almost two thiol groups at the terminals.

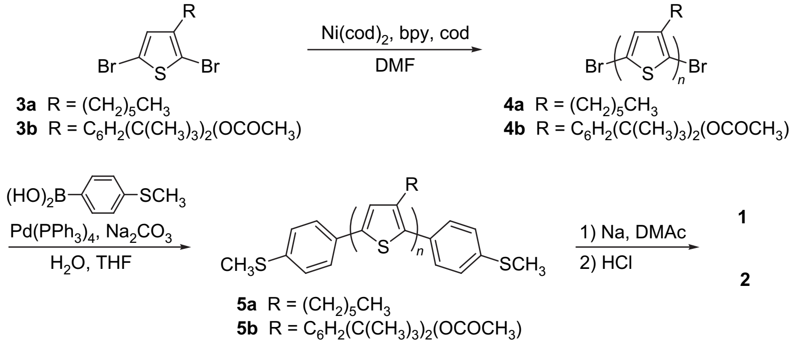
The deprotection reaction of the thiol precursor groups at the terminals of the polythiophene backbone was carried out quantitatively using sodium. The structure and electronic state of the obtained thiol group-terminated polythiophenes, **1** and **2**, after treatment with hydrochloric acid were similar to those of the precursor polythiophenes **5a** and **5b**, respectively.

The TEM and TGA analyses of the tetraoctylammonium bromide-stabilized gold nanoparticle **AuNP** revealed that the diameter and the content of gold were 3.3 ± 0.8 nm and 86%, respectively, representing that the number of gold atoms and stabilizing molecules per nanoparticle were ca. 1040 atoms/particle and 270 molecules/particle, respectively.

A 0.4 wt% suspension of **AuNP** in toluene was mixed with an equal volume of the thiol group-terminated polythiophene **2** toluene solution (4.0 wt%). Molar ratio R of the thiol groups in **2** (ca. 1.2×10^{19} molecules in 1.0 ml of 4.0 wt% toluene solution) against the surface gold atoms of **AuNP** (ca. 2.7×10^{18} atoms in 1.0 ml of 0.4 wt% toluene suspension) was calculated to be around 4, by considering the molecular weight of the polythiophene ($M_w = 4000$) and the number of gold atoms and surface atoms per nanoparticle (ca. 1040 atoms/particle and 270 surface atoms/particle, respectively). A black film was formed on the electrodes by S–Au bond formation between the thiol group of polythiophene and the gold nanoparticle. The obtained film was insoluble in any solvent, and adhered to the electrodes even after washing by ultrasonic cleaner, indicating S–Au bond formation between the gold electrode and the polymer. Fig. 1(a) shows the cross-sectional FE-SEM images of the polythiophene/gold nanoparticle network film (**2/AuNP**) on a micro comb-shaped gold electrode with a gap of 5 μm. The TEM sample was prepared on a copper-grid by skimming off a floating insoluble film from the mixture solution of **2** and **AuNP**: the TEM image showed the assembly of 3.3 ± 0.8 nm-sized gold nanoparticles maintaining nearly-constant intervals (4.6 ± 0.9 nm) from one another, suggesting that the thiol group-terminated polythiophene molecules (molecular length of **2** for 13-mer = ca. 4.8 nm) were located among the gold nanoparticles (Fig. 1(b)). The network film composed of **1** and **AuNP** was also prepared with similar morphology.

Fig. 2(a) is an XPS spectrum of **2** at the region of narrow scan on sulfur S 2p. Each signal at binding energies of 163.6 eV (S $2p_{3/2}$) and 164.9 eV (S $2p_{1/2}$) was derived from a mixture of the free thiol groups (S–H) and the thiophene of **2**. On the other hand, S 2p signals of the network film **2/AuNP** were detected at 161.9, 162.9, 163.7, and 164.8 eV (Fig. 2(b)). The S 2p signals with lower binding energies (161.9 and 162.9 eV) and other signals (163.7 and 164.8 eV) were ascribed to sulfur bound with the gold nanoparticle (S–Au) and sulfur in the thiophene, respectively [17]. These microscopic and XPS results support the formation of the alternate network structure of the thiol group-terminated polythiophene and gold nanoparticle through the conjugated S–Au bond linkage.

The electric conductivity σ of each sample was measured with the I–V measurements using micro comb-shaped electrodes. The electric conductivity of **2/AuNP** ($\sigma = 1.9 \times 10^{-6}$ S/cm) was much higher than those of **4b**, **5b**, and the simply mixed **5b/AuNP** ($\sigma = 10^{-11}$–10^{-10} S/cm) (Table 1). The activation energy E_a of the electric conductivity was estimated by Arrhenius plots ($\ln(\sigma)$–$1000/T$)



Scheme 1. Synthesis of the thiol group-terminated polythiophenes.

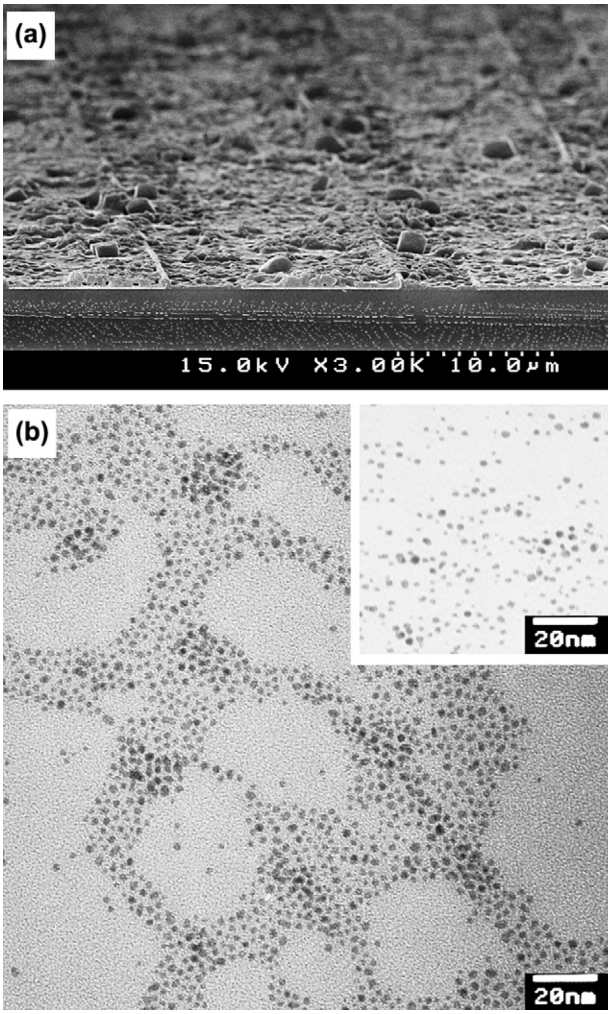


Fig. 1. (a) SEM image of the **2/AuNP** network film on the gold micro comb-shaped electrode with a gap of 5 µm. (b) TEM image of the **2/AuNP** network film. (Inset: TEM image of the **AuNP**.)

(Fig. 3). The network film **2/AuNP** showed an excellent conductive characteristic with $E_a = 12.0$ meV, which was much lower than those of **4b**, **5b**, and **5b/AuNP** (Table 1). These results indicate that the polythiophene/gold nanoparticle alternate network structure with S–Au conjugated linkages is effective for conductivity enhancement. Morphology and chemical binding information of the network films after conductivity measurement were also examined by microscopy and XPS, which result in similar images and spectra to Figs. 1 and 2, respectively.

Here we discuss about the conductive mechanism of the network film by comparing the conductive characteristics of the alternate network films composed of alkanedithiol and gold nanoparticles. The electric conductivity and activation energy varied with the length of the alkanedithiol molecules; the network film with a longer alkanedithiol shows lower conductivity and higher activation energy (hexanedithiol/**AuNP**: $\sigma = 7.6 \times 10^{-6}$ S/cm and $E_a = 15.3$ meV, decanedithiol/**AuNP**: $\sigma < 10^{-8}$ S/cm and $E_a = 19.2$ meV, and dodecanedithiol/**AuNP**: $\sigma < 10^{-8}$ S/cm and $E_a = 63.5$ meV). This tendency agrees with a previously reported result [18], in which the electric conductive mechanism of the gold nanoparticles connected with the aliphatic molecules was considered to be a thermal hopping among the gold nanoparticles. The activation energy of **2/AuNP**, however, is lower than that of dodecanedithiol/**AuNP**, even though the molecular length of **2** (ca. 4.8 nm) is several times longer than that of dodecanethiol (ca. 1.9 nm). This result suggests that the conductive characteristic of the polythiophene/gold nanoparticle network film originated from that of the π-conjugated polythiophene backbone connected with the gold nanoparticle.

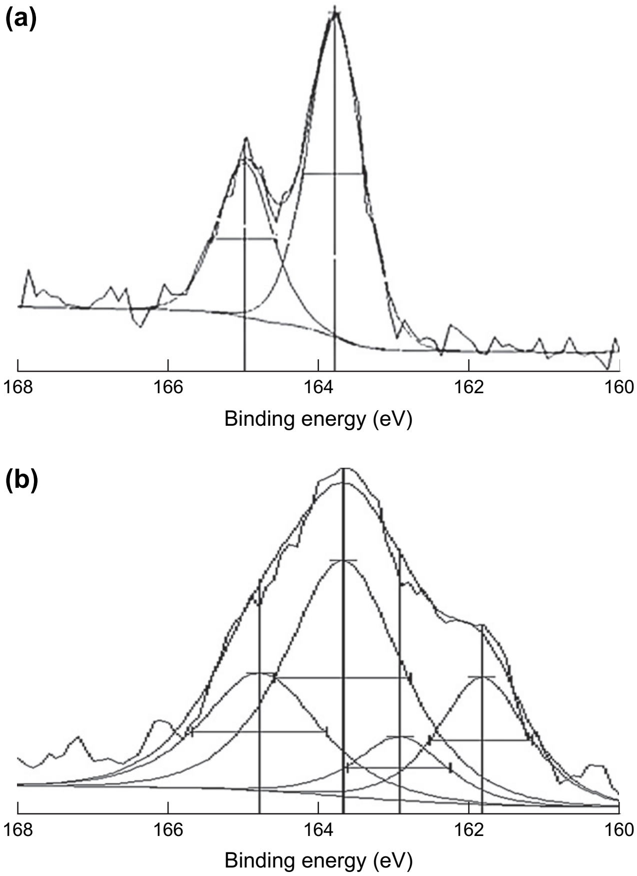


Fig. 2. XPS spectrum of (a) **2** and (b) **2/AuNP** at the region of the narrow scan on sulfur S 2p.

The conductive characteristic of **2/AuNP** was superior to that of **1/AuNP**, despite their molecular length and film morphology being almost identical to each other. The reason why there is a difference in their conductive characteristics

Table 1
Conductive characteristics of the polythiophene and the network films

Entry	Sample	Solvent-solubility of the film	Electric conductivity[a] σ (S/cm)	Activation energy E_a (meV)
1	**4b**	Soluble	3.7×10^{-11}	320
2	**5b**	Soluble	7.9×10^{-11}	260
3	**5b/AuNP**	Soluble	5.3×10^{-11}	250
4	**2/AuNP**	Insoluble	1.9×10^{-6}	12
5	**1/AuNP**	Insoluble	2.3×10^{-7}	180

[a] At 300 K.

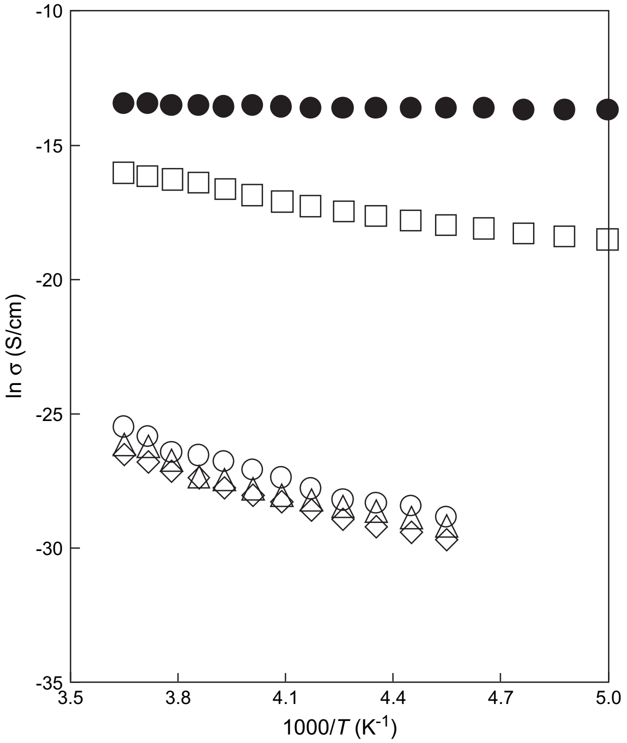


Fig. 3. Arrhenius plots (ln(σ)−1000/T) of **4b** (◇), **5b** (○), **5b/AuNP** (△), **1/AuNP** (□), and **2/AuNP** (●).

is considered to be due to the fact that the bearing bulky group of **2** contributed to the elongation of the effective conjugated length of the polythiophene backbone by preventing the coordination of the polythiophene backbone to the gold nanoparticle. Another possible factor to affect the conductive characteristic of **2** is that a part of the bearing phenol derivative was oxidized by air to generate a phenoxyl radical. The network film **2/AuNP** was allowed to stand for a long time to quench the incidentally generated radical: the conductivity of the sample was around 10 times lower than that of the pristine one, suggesting possible effect of radicals on the conductivities. The contribution of a radical's unpaired electron on the electric conductivity of the conjugated polymer was theoretically predicted [19] and had been experimentally demonstrated with a bulk phenoxyl radical-bearing polythiophene film in our previous study [14].

In conclusion, the polythiophene/gold nanoparticle alternate network film was prepared by mixing the thiol group-terminated polythiophene and the gold nanoparticle. The excellent conductive characteristics of the network film, relatively high electric conductivity and extremely low activation energy demonstrate that the intrinsic conductive characteristic of the polythiophene backbone can be evaluated by connecting the polythiophene with gold nanoparticles through the linkage of conjugated S−Au bonds.

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