Toward the high efficiency organic solar cell with a vertical p-n junction structure
垂直 p-n 界面制御による有機薄膜太陽電池の高効率化

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1. Introduction

Si-based solar cells have been utilized in many occasions as a renewable energy source; however, it has been impossible to replace other conventional nonrenewable energy sources with the solar cells because its manufacturing cost is much higher than that of other nonrenewable energy sources. The organic based solar cells, on the other hand, can possibly offer special opportunities as a renewable energy source because they can be fabricated over large area using low cost printing technologies. The progress in the field of the polymer based solar cells has been promising with the recently reported power-conversion efficiency of ~6%. Although it is still ineffective to be the technology utilized in commercial products, there could be plenty of room for the improvement in the power-conversion efficiency of the polymer based solar cells. In this research, we will present the synthesis methodology to produce high mobility polymers that can possibly be utilized in polymer-based solar cells with improved power-conversion efficiency.

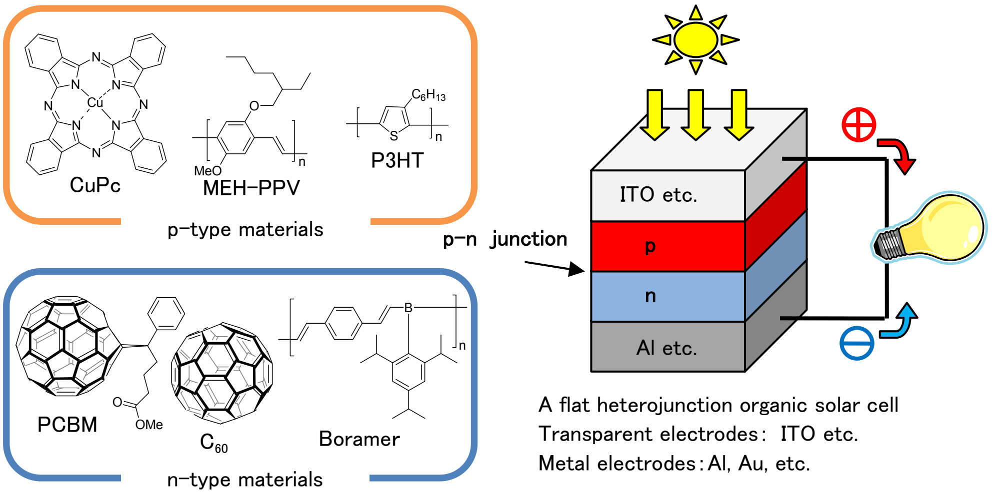
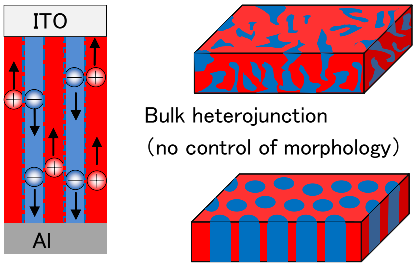


Fig.1 Basic principle of organic based solar cells.

It is important to understand how organic or polymer based solar cells work to improve its power-conversion efficiency. A simple organic solar cell has the planer structures shown in the Figure 1, and the structure is very similar to that of the Si-based solar cells with the p-n junction sandwiched with the transparent conductor such as ITO and metal electrodes. The working principle is also similar to each other. The photo excited species are generated in the p- or n-type semiconductor materials, and they are separated as holes and electrons at the p-n junction. To take out energy from a solar cell, the separated holes and electrons have to be collected at the electrodes. Thus, the materials need to satisfy the following criteria to be a good solar cell material: 1) high absorption of light; 2) efficient charge separation; 3) sufficient charge transport. We have proposed the nanowire based vertical p-n junction structure shown in the figure 2 to satisfy all these criteria.



Bulk heterojunction
(no control of morphology)

Vertical p–n junction
(controlled morphology)

Fig 2. Vertical p–n junction

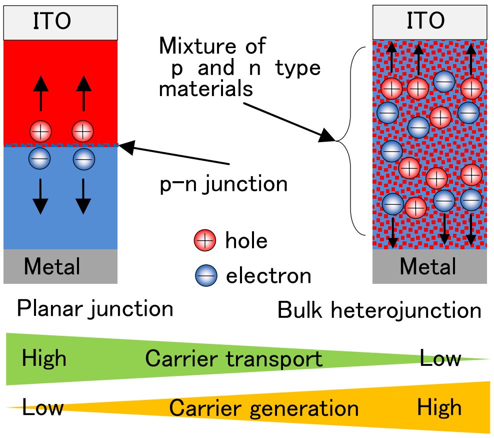


Fig 3. Carrier generation and transport

The polymer based organic solar cells with the best power-conversion efficiency reported so far has the structure named bulk heterojunction, in which photo excited species have chance to be separated as holes and electrons anywhere in the device because the p-n junction is distribute all over the mixture of the p- and n-type materials (Fig. 3). The device structure can possibly account for the two criteria; high absorption of light and efficient charge separation, however, the charge transport cannot be controlled. In contrast, the vertical p-n junction device structure can satisfy all these criteria (Fig. 3).

In the construction of the polymer based organic solar cells with the vertical p-n junction structure (Fig. 2), it is important to have the polymeric nanowires with high carrier mobility because carriers will need to travel long distance along the nanowires to the electrodes. With the invention of such high mobility polymer structures, one can possibly fabricate the vertical p-n junction solar cell structures following a simple fabrication scheme (Fig.4). Here we demonstrate the synthesis of such high mobility polymeric nanowires through a template synthesis of PEDOT. The nanowires of PEDOT have been synthesized within the nano-sized template (Anodic Alumina Oxide, AAO, Fig. 5), and the resulting nanowire's nanostructure was characterized using SEM and TEM. The chemical, electrical, and structural properties of the nanowires were also characterized using EDX, 4-wire conductivity measurement, and Raman spectroscopy, respectively. These characterizations revealed that the AAO template grown PEDOT nanowires have improved mobility, being suitable material for the construction of the polymer based vertical p-n junction organic solar cells.

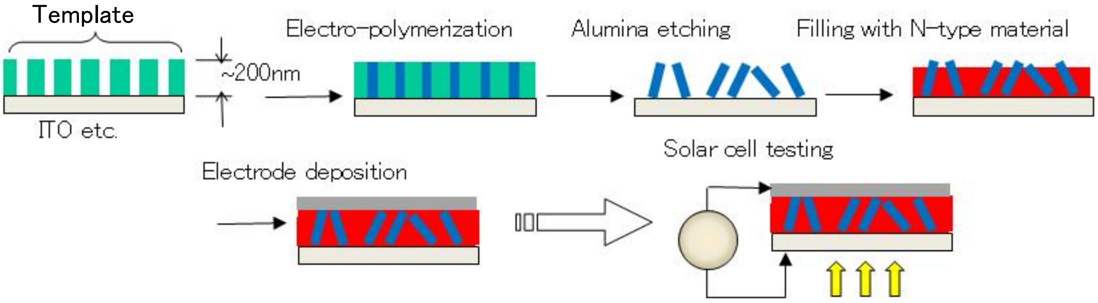
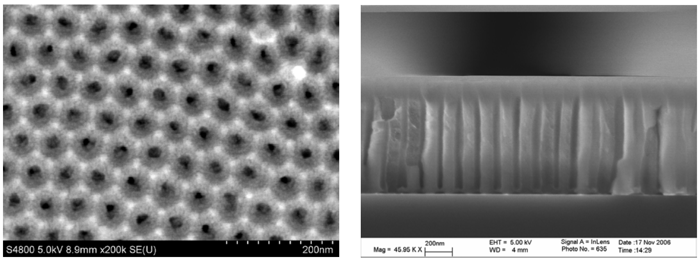


Fig.4 Fabrication scheme for the polymer based organic solar cell with a vertical p-n junction using high mobility polymeric nanowires.



Top view of AAO template Cross-section of AAO template

Fig.5 Structure of AAO template

2. Experimental

3,4-Ethylenedioxythiophene (EDOT) and anhydrous acetonitrile (CH_3CN) were obtained from Aldrich. Lithium perchlorate ($LiClO_4$) was obtained from Wako. Gold electroplating solution (Galvanomeister GB3) was purchased from Tanaka Kikinzoku. AAO membrane with a pore diameter of 0.2 μm and a thickness of about 60 μm (Anodisc 13) was obtained from Whatman. Deionized water was obtained by using a Milli-Q water purification system from Millipore.

AAO templates with small pore diameters (50 and 100 nm) were fabricated by using a two-step anodization process.[1] An Al sheet (15 ×15 × 0.5t, 99.99%) was anodized for about 18 h at 40 V and 10 °C by using 0.3 M oxalic acid as an electrolyte to fabricate AAO membranes with a pore diameter of 50 nm. For AAO membranes with 100 nm pores, Al sheets were anodized for about 18 h at 100 V and 0 °C by using 0.15 M oxalic acid as an electrolyte, and an anodization current was limited below 350 mA to avoid an excessive heating of anodizing samples. The anodization process was repeated after the removal of the irregular pores produced in the initial anodization process to make a well-defined pore structures. Thus, the initially formed alumina pores were removed by placing the Al sheets with alumina pores in an aqueous mixture of phosphoric acid and chromic acid at 60°C for about 5 h. The second anodization was performed for 18 h and 5.5 h for 50 nm and 100 nm pore samples, respectively. The aluminum layers left after the anodization process were removed using an acidic copper chloride solution. The removal of alumina barrier layer and pore-widening were performed by using phosphoric acid (10 wt %) at 30 °C.

Electropolymerization of EDOT was performed following the method developed by Lee et al. with the following modifications.[2] EDOT was polymerized at a constant current density of 1 mA/cm^2 with a galvanostatic mode in a three electrode configuration using a Pt counter electrode and an Ag/AgCl reference electrode. The concentration of EDOT was 1.0 M, and the electrolyte solution was 0.1 M $LiClO_4$ in acetonitrile. For a working electrode, one side of an AAO membrane with nanopores was coated with a thin layer of Au (~300 nm) by using a sputtering system operating at 200W, and Au plating was performed by galvanostatically repeating the -1.0 A/dm^2 (0.1 s) and +8.0 A/dm^2 (0.01 s) to completely fill the bottom of the nanopores with gold.

SEM, TEM, and Raman spectroscopy characterization of the nanowires were performed by releasing the nanowires into solution by dissolving the AAO template in 1.0 M KOH, and casting the nanowire sample solution on to a Si substrate or TEM grid. The samples were repeatedly centrifuged and rinsed in water to remove the KOH before the casting. Electrical measurements on the PEDOT nanowires were performed using a 4-wire resistivity measurement method. The nanowire solution was casted on the Si substrate with patterned 4-wire Au electrodes fabricated using lithography.

3. Results and Discussion

Synthesis of the PEDOT nanowires. The nanowires were grown using a conventional 3-electrode configuration (Fig 6). By applying the enough potential on the Au electrode at the bottom of the AAO template, the PEDOT was successfully oxidized at Au electrode surfaces and formed nanowire shaped polymeric structures in the AAO template. AAO template with the three different pore diameters of 50, 100, and 200 nm were used in this study.

Characterization of polymer nanostructures. It is important to observe and understand the nanostructures of synthesized PEDOT polymers before investigating their electrical performance in organic solar cells because the cell performance will strongly depend on the nanostructure of the polymers. Thus, the

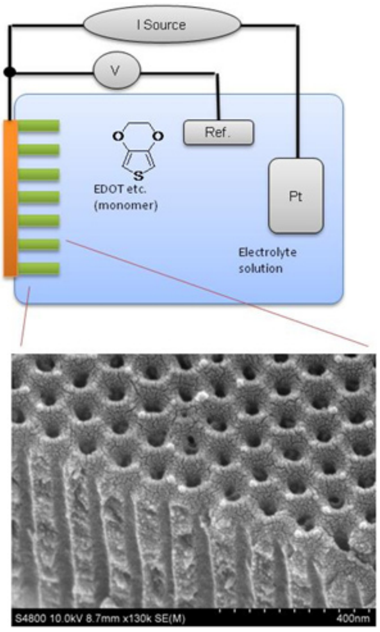


Fig.6 Configuration for the templated electrochemical polymerization of the PEDOT nanowires.

template grown polymeric nanowires were investigated using SEM and TEM. The PEDOT nanowires were released from the AAO template, and the SEM images (Fig.7) on individual PEDOT nanowires revealed that the nanowire diameter can be controlled by changing the size of the pore diameters in the AAO template. TEM observation confirmed the formation of the completely filled nanowires.

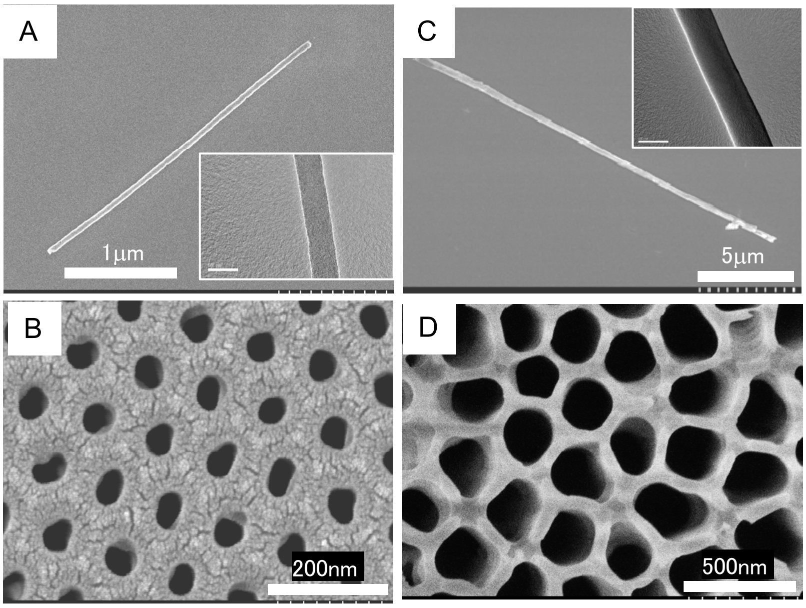


Fig.7 SEM and TEM images of PEDOT nanowires and AAO templates. (A, B) 50 nm PEDOT nanowire and AAO template. (C, D) 200 nm PEDOT nanowire and AAO template. Inset shows TEM images of nanowires with white bars indicating 50 nm and 200 nm.

Electrical measurement on the PEDOT nanowires. The conductivity of the PEDOT nanowires synthesized using three different AAO template sizes (50, 100, 200 nm) was estimated using a 4-wire resistivity measurement technique (Fig. 8). By applying a small amount of current going through the nanowire, a voltage drop across the nanowire was measured using a voltmeter. Over 100 samples of the PEDOT nanowires made with three different AAO templates were measured, and the results were summarized in the Figure 9. It has been revealed that the PEDOT nanowire conductivity will increase as the decrease of the nanowire diameters. This

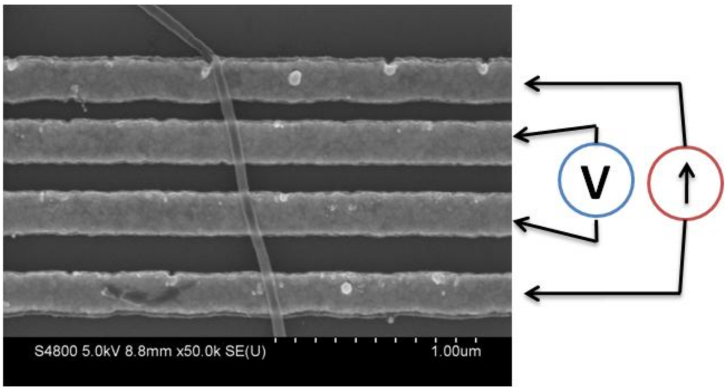


Fig.8 4-wire resistivity measurement on PEDOT nanowires. SEM image of a 50 nm nanowire bridging four Au electrodes being measured using a 4-wire resistivity measurement technique.

result strongly suggests that there are some chemical and/or structural changes in the nanowires. The material's conductivity (σ) is generally known to be proportional to the product of the carrier density (n) and the carrier mobility (μ), and can be expressed as:

$$\sigma \propto n \cdot \mu \qquad (1)$$

From this relationship, it is possible to determine which factor is the dominant source in the conductivity enhancement in the PEDOT nanowires with smaller diameters. To answer this question, we have explored the carrier density of the nanowires with EDX and the structural properties of nanowires using Raman spectroscopy methods.

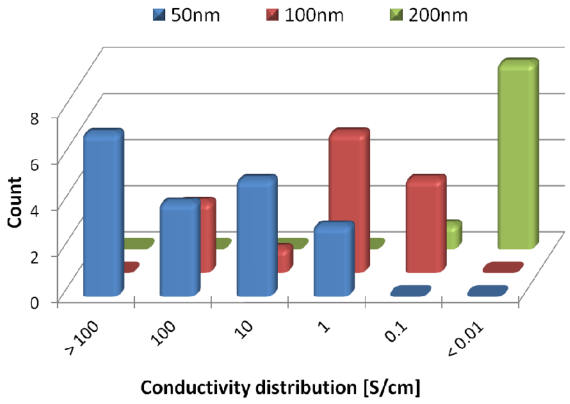


Fig.9 Conductivity distribution of the PEDOT nanowires synthesized using the AAO template with 50, 100, and 200nm sizes.

EDX analysis on the chemical composition of the PEDOT nanowires. The electrical properties and conductivity of a conducting polymer will strongly depend on the extent of the doping. Thus, it is crucial to determine the amount of the doping materials within the PEDOT nanowires, and the result is directly related to the carrier density of the material. Because the electrochemical polymerization was conducted using $LiClO_4$ as an electrolyte, the ClO_4 anion will be incorporated into the polymer matrix as a dopant, and the extent of the doping can be estimated from the atomic concentration ratio of the sulfur atom in the PEDOT to the chlorine atom in the ClO_4 anion. The estimated doping of the nanowires with the three different diameters is listed in the table 1. It is clear that the doping of the nanowires remains constant and has no diameter dependence. This result strongly suggests that the carrier density of the PEDOT nanowires has no role in the measured conductivity enhancement of the nanowires with smaller diameters.

Table 1. Doping density estimation using EDX.

Nanowire diameter	Atomic Concentration ratio: S/Cl	Extent of doping
50 nm	23.3	4.3%
100 nm	21.7	4.6%
200 nm	23.4	4.3%

Raman analysis. According to the equation (1) and the EDX analysis results, the huge conductivity enhancement in the small diameter PEDOT nanowires is due to the increase in the carrier mobility in the nanowires. An improvement in the carrier mobility usually reflects the enhanced supramolecular structure and/or the formation of better crystal structural order within the materials. Thus, we have carried out Raman analysis on our PEDOT nanowires to examine the polymer morphologies. The Raman spectra of PEDOT nanowires recorded using Ar+ 514.53 nm, laser excitation line, are shown in Figure 10. Examination of the 1300–1600 cm^{-1} spectral region shows that in general the peaks are relatively more intense for the 50 nm PEDOT than for 200 nm PEDOT nanowires. The most intense peak at 1427 cm^{-1} is assigned to the symmetric stretching mode of the C=C double bonds, whereas a less intense peak at 1508 cm^{-1} is characteristic of the C=C antisymmetric stretching vibration.[3] Other weaker peaks at 1361 and 1262 cm^{-1} are attributed to the stretching mode of single C-C bond and the C-C inter-ring bonds, respectively.[3] Other very weak bands at 600 to 700 cm^{-1}, related to defects in the polymer chains, and around 1100 cm^{-1}, related to distorted C-C interring bonds of the polymer chains, suggest that the polymer chains in nanowires present a highly planar structure for all the diameter PEDOT nanowires. It has been theoretically and experimentally studied that the conjugation length of the polythiophenes is strongly correlated with the abundance of coplanar segments. Sauvajol et al. reported using polythiophene films that the symmetric C=C stretching mode is narrowing when the conjugation length increases.[4] Indeed, a careful examination of the intense line at 1427 cm^{-1} revealed the line narrowing as the nanowire diameter decreases (Fig. 10). This result strongly suggests the enhancement in conjugation length in the smaller diameter nanowires, and this finding supports the mechanism of the conductivity enhancement. The polymer morphology can be strongly enhanced in the polymerization process within the nano-sized AAO templates.

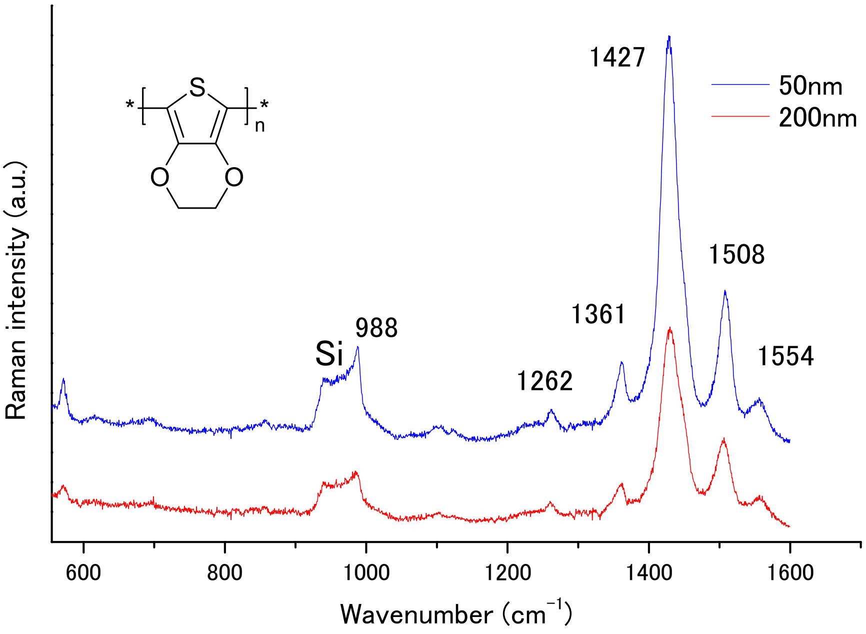


Fig.10 Raman spectra of PEDOT nanowires synthesized in AAO template with 50 and 200 nm pore sizes. A broad band at around 900 to 1000 cm−1 is due to a Si substrate.

4. Conclusion

We have demonstrated the synthesis of the high mobility polymeric nanowires through a polymerization using AAO templates. The nanowires of PEDOT have been synthesized within the nano-sized AAO template (Fig. 5), and the resulting polymer nanostructure was characterized using SEM and TEM. The chemical, electrical, and structural properties of the nanowires were also characterized using EDX, 4-wire conductivity measurement, and Raman spectroscopy, respectively. These characterizations revealed that the AAO template grown PEDOT nanowires have improved carrier mobility, being suitable material for the construction of the polymer based vertical p-n junction organic solar cells. We are now taking a next step toward the realization of the solar cells using the materials and methodologies developed in this research. This work was supported by the JFE 21st Century Foundation.

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