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Design and Performance of Electrospun
sp²-Carbon Based Active Layer and Flexible
Gas Barrier Film in Photovoltaic Devices

전기 방사된 sp²-탄소 기반 활성층과 유연성 기체 차단성
필름으로 구성된 태양전지 설계 및 성능 평가

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Abstract

Design and Performance of Electrospun sp$^2$-Carbon Based Active Layer and Flexible Gas Barrier Film in Photovoltaic Devices

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This thesis described the design and performance of next generation flexible photovoltaic devices based on sp$^2$-carbon materials for high power conversion efficiency and stability. Photovoltaic devices are capable of converting solar energy into electrical energy, and act as future-oriented energy harvesting devices. Organic photovoltaic devices based on sp$^2$-carbon materials including nanocarbon and conjugated polymers are preferred over conventional photovoltaic devices due to their
solution-processable nature, low cost, and flexibility. However, the organic photovoltaic devices are accompanied by issues in efficiency and lifetime. Therefore, it is highly important to develop organic photovoltaic devices with enhanced power conversion efficiency and long stability. The aim of this study is to identify the factors that can be varied in order to achieve these requirements by examining the theoretical considerations, and then to design the photovoltaic devices for high efficiency and long lifetime.

Part I provides a general introduction regarding $sp^2$-carbon materials and organic photovoltaic devices. Using theoretical considerations and state of the art analysis, the factors for photovoltaic devices with high efficient and long lifetime are extracted. The aims of the present work are introduced on the basis of these derived factors.

In Part II, with the aim of enhancing power conversion efficiency, organic photovoltaic cell based on one-dimensional conjugated polymers is prepared. Electrospinning techniques are used to prepare conjugated polymer nanofibers and photovoltaic devices in ambient air, regardless of relative humidity condition. The diameters of the conjugated polymer nanofibers are approximately twice the exciton diffusion length, 20nm. The short circuit current and power conversion efficiency of the device increased to 11.54 mA/cm$^2$ and 5.82 %, respectively. The suggested method can be applied to the fabrication, in ambient air, of large-area active layers composed of other new conjugated polymers to yield high-performance OPV devices.

Part III discusses the preparation and properties of reduced graphene oxide-based gas barrier films for the enhancement of the stability of organic photovoltaic devices. The simple and direct spin-casting of a graphene oxide suspension on an aluminum electrode is performed to encapsulate the OPV device with reduced graphene oxide film. The lifetime of the OPV device after the reduction process was increased by 100
times compared to an unencapsulated OPV device. Furthermore, the gas barrier property is enhanced more by controlling the thermal reduction condition. The gas barrier property is closely related to the surface roughness, dispersibility and reduction condition of graphene oxide. Flexible photovoltaic devices encapsulated by the reduced graphene oxide-based gas barrier film are prepared. The reduced graphene oxide allows a long lifespan while maintaining flexibility. Further investigations of the preparation and reduction of the graphene oxide film would improve the performance.

**Keywords:** photovoltaic, carbon nanomaterials, electrospinning, conjugated polymer, nanofiber, flexible device

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Contents

Part I Basic research for organic photovoltaic devices

Chapter 1. Introduction............................................................... 2

1.1 General introduction to photovoltaic devices ....................... 2

1.1.1 Overview of photovoltaic devices .................................. 2

1.1.2 Demand for generation photovoltaic devices .................... 5

1.1.3 Next-generation photovoltaic devices: sp2-carbon-based organic photovoltaic devices ......................................................... 6

1.2 Theoretical consideration for the sp2-carbon-based photovoltaic devices ................................................................. 9

1.2.1 Review of carbon-based electronic materials .................... 9

1.2.1.1 Carbon nanomaterials .............................................. 9

1.2.1.2 Conjugated polymers ................................................ 17
1.2.2 Structure of the organic photovoltaic devices ..................................... 20

1.2.2.1 Transparent electrode ........................................................................... 22

1.2.2.2 Hole transport layer .............................................................................. 24

1.2.2.3 Active layer .......................................................................................... 24

1.2.2.3.1 Formation of excitons in a polymer .................................................. 24

1.2.2.3.2 Heterojunction structure ................................................................. 26

1.2.2.3.3 Limited exciton diffusion length in a polymer ................................. 26

1.2.2.3.4 Bulk heterojunction structure ......................................................... 27

1.2.2.4 Cathode ................................................................................................ 27

1.2.2.5 Encapsulation layer ............................................................................. 28

1.3 State-of-the-art works on organic photovoltaic devices ..... 28

1.3.1 High-performance devices ...................................................................... 28

1.3.1.1 Synthesis of a new conjugated polymer ............................................. 29

1.3.1.2 Synthesis of a new acceptor ................................................................. 29

1.3.1.3 Control of the morphology ................................................................. 30
1.3.1.3.1 Conventional method to control the morphology of the active layer ................................................................. 30
1.3.1.3.2 Rational morphology control by 1D conjugated polymers ...... 34
1.3.2 Long-lifetime devices ................................................................. 42
   1.3.2.1 Encapsulation design .......................................................... 42
   1.3.2.2 Inverted solar cell .............................................................. 42
1.4 Aim and scope of this research .............................................. 45
   1.4.1 Efficiency enhancement of photovoltaic devices ......................... 45
      1.4.1.1 Issue: Limited materials that form self-assembled nanowire ...... 45
      1.4.1.2 Preparation and characterization of P3HT nanofibers ............... 46
      1.4.1.3 Preparation of highly reproducible photovoltaic devices based on P3HT nanofibers ......................................................... 46
      1.4.1.4 Performance of photovoltaic devices based on PCDTBT nanofibers .................................................................................. 46
   1.4.2 Preparation of flexible and long-lifetime photovoltaic devices ....... 47
      1.4.2.1 Issue: incompatibility of conventional encapsulation methods and
1.4.2.2 Preparation and characterization of flexible gas barrier film

1.5 References
Part II Design and Performance of a Nanoweb of a Conjugated Polymer-Nanofiber-Based Active Layer for High-Performance Photovoltaic Devices

Chapter 2. Preparation and Characterization of Electrospun Conjugated Polymer Nanofibers .......... 54

2.1. Introduction ........................................................................................................... 54

2.2. Experimental section ......................................................................................... 58

2.2.1. Chemicals and materials ................................................................................ 58

2.2.2. Electrospinning ............................................................................................... 58

2.2.3. Characterization ............................................................................................. 59

2.2.4. PL test ............................................................................................................. 59

2.3. Results and discussion ....................................................................................... 61

2.3.1. Control of the diameters of the P3HT nanofibers ....................................... 61

2.3.2 Optical properties of the nanofibers ............................................................... 82

2.3.3. Photoluminescence quenching ..................................................................... 86
Chapter 3. Highly Reproducible Electrospun
Conjugated Polymer Nanofibers Based Photovoltaic
Devices .............................................................. 93
Chapter 4. Preparation and Performance of PCDTBT Nanofibrous Photovoltaic Devices ......................... 126

4.1. Introduction ................................................................ 126

4.2. Experimental Section ................................................... 128

4.2.1. Chemicals and materials ........................................... 128

4.2.2. Fabrication and characterization of the nanofibers .......... 128

4.2.3. Fabrication and characterization of the OPV devices .......... 129

4.3. Result and Discussions ................................................. 131

Figure 4.1. Schematic diagram showing the preparation of a nanofibrous OPV device...................................................... 132

Figure 4.3. The viscosities of the spinning dope solutions. ............ 137

4.4 Conclusions .................................................................. 168

4.5. References ................................................................... 169
Part III Design and Performance of a Carbon-Nanomaterial-Based Encapsulation Layer and Electrodes for Flexible Photovoltaic Devices

Chapter 5. Preparation and Characterization of Reduced Graphene Oxide Based Encapsulation Film

5.1. Introduction ................................................................. 174

5.2. Experimental ............................................................... 176
  5.2.1. Preparation of the GO solution ...................................... 176
  5.2.2. Fabrication and characterization of OPV devices ............. 176
  5.2.3. Preparation and characterization of the rGO film .............. 177
  5.2.4. Fabrication of a flexible OPV device .............................. 177

5.3. Results and discussion .................................................. 178
  5.3.1. Direct preparation of rGO films on OPV devices for encapsulation ......................................................... 178
  5.3.2. Preparation of flexible rGO-based encapsulation films ........... 192
5.4. Conclusion ................................................................. 211
5.5. Reference ................................................................. 212
Chapter 6. Concluding remarks ..................................... 214
List of Tables

Table 1.1. List of various materials for transparent conducting films

Table 2.1. Morphological characteristics and average diameters of electrospun P3HT@PEO and F8BT@PEO composite nanofibers

Table 2.2. The PEO residues in the P3HT@PEO composite nanofibers after dipping into various solvents maintained at temperatures above 70 °C

Table 3.1. Variations in the diameters of the electrospun fibers and beads as a function of the RH.

Table 3.2. Performances of the OPV devices prepared using PCDTBT nanofibers with various diameters.

Table 3.3. Variations in the solvent evaporation rate under different RH conditions.

Table 3.4. Performance properties of the OPV devices prepared using PCDTBT nanofibers with various diameters.

Table 4.1. Specific surface area and pore volume in the materials, characterized according to the N₂ adsorption isotherms (at 77K).

Table 4.2. Performance details of the OPV devices composed of PCDTBT nanofibers with various diameters.
Table 4.3. Performance details of the BHJ, pseudo-bilayer, and nanofibrous structured OPV devices

Table 5.1. BET SSA and pore volume in the materials, characterized according to the N₂ adsorption isotherms (at 77K)

Table 5.2. WVTR value of PEN and PEN/rGO films as characterized by the MOCON instrument
List of Figures

Figure 1.1. Estimation of (a) primary energy consumption and (b) renewable energy consumption.

Figure 1.2. Generation cost for electricity from various energy sources.

Figure 1.3. The carbon atoms form 0D fullerene, 1D CNT, 2D graphene, and 3D graphite structures.

Figure 1.4. Molecular structure of fullerenes and their derivatives.

Figure 1.5. Chiral vector on unrolled graphene sheet. The vectors OA and OB are the chiral and translational vectors, respectively.

Figure 1.6. Molecular structures of CNTs and functionalized CNTs.

Figure 1.7. Preparation method of reduced graphene oxide.

Figure 1.8. Molecular structure of representative conjugated polymers.

Figure 1.9. Device structure of OPV devices.

Figure 1.10. AFM image of (a) CNTs based transparent conducting electrode and (b) graphene film. (d) SEM image of silver nanowires based electrode.

Figure 1.11. TEM images of a P3HT:PC_{60}BM film (a) before and (b) after thermal annealing.

Figure 1.12. Influence of film growth rate on the carrier mobility.

Figure 1.13. Scheme of (a) single layer structure (b) bilayer structure (c) BHJ
structure and (d) ordered heterojunction structure.

**Figure 1.14.** AAO template-based nanotechnology, (a) after the infiltration of TiO2, (b) cross-sectional image of (a), (c) after the removal of AAO, and (d) cross-sectional image of (c).

**Figure 1.15.** (a) Scheme of P3HT nanorod/fullerene structure OPV device. SEM images of (b) top and (c) side views of AAO template and (d) P3HT nanorods.

**Figure 1.16.** (a) SEM and (b) AFM images of P3HT nanowire obtained by self-assembly method.

**Figure 1.17.** OPV devices of the normal (top) structure and inverted (bottom) structure.

**Figure 1.18.** Scheme of the sp²-carbon based OPV device and aim of chapters.

**Figure 2.1.** SEM micrographs of fibers electrospun from spinning dope solutions in chloroform containing (a) 1 wt% P3HT only; PEO only: (b-1) 1 wt%, (b-2) 0.5 wt%, (b-3) 0.25 wt%; P3HT@PEO mixtures: (c-1) 1/1 wt%, (c-2) 0.5/0.5 wt%.

**Figure 2.2.** Variations in the diameters of the electrospun fibers with the PEO concentration of the spinning dope solutions.
**Figure 2.3.** The variations in the conductivity of the spinning dope solution and the diameter of the electrospun nanofibers of PEO with the concentration of DMF/acetic acid in the polar cosolvent mixture in the spinning dope solution (concentration of PEO: 0.35 wt%).

**Figure 2.4.** SEM micrographs of the electrospun PEO nanofibers for various concentrations of DMF/acetic acid in the polar cosolvent mixture: (a) 5 wt%, (b) 8.3 wt%, (c) 10 wt%, (d) 13.3 wt%, (e) 16.6 wt%, and (f) 18.3 wt% (concentration of PEO: 0.35 wt%).

**Figure 2.5.** SEM micrographs of electrospun P3HT@PEO composite nanofibers with various P3HT/PEO ratios (in wt%): (a) 0.15/0.35, (b) 0.25/0.35 (inset: a magnified image with a scale bar of 100 nm), and of electrospun F8BT@PEO composite fibers with various F8BT/PEO ratios (in wt%): (c) 0.25/0.35, (b) 0.15/0.35.

**Figure 2.6.** (a) STEM micrograph of electrospun P3HT@PEO composite nanofiber and (b) EDS mapping with the intensity graph of carbon (green), sulfur (red yellow) and oxygen (purple) on selected area of (a).

**Figure 2.7.** Dependence of energy dissipation rate on the viscosity ratio $H = \eta_{\text{low}}/\eta_{\text{high}}$ between the two polymers.
**Figure 2.8.** Thermo-gravimetric thermograms of various samples under isothermal treatment at 370 °C.

**Figure 2.9.** SEM micrographs of electrospun virgin P3HT fibers. (a-b) Low and high magnification images (inset: scale bar 100 nm), and (c-d) larger diameter P3HT electrospun fibers.

**Figure 2.10.** UV-Visible absorption spectra of (a) virgin P3HT fibers (red dashed line) and a P3HT film (black solid line) and (b) virgin F8BT fibers (red dashed line) and a F8BT film (black solid line) (inset: spectra magnified in the range 440~500 nm). (Normalized with respect to maximum intensity of each graph, scattering effect was corrected using PEO fibers).

**Figure 2.11.** XRD patterns of the virgin P3HT nanofibers (black) and the spin-cast P3HT film (red).

**Figure 2.12.** PL quenching properties of virgin P3HT nanofibers with various diameters: P3HT nanofibers only (80 nm, black squares); composite films of PC$_{60}$BM with P3HT nanofibers (460 nm, red circles; 290 nm, green triangles; 80 nm, blue triangles).

**Figure 3.1.** J-V curves obtained from the electrospun OPV devices prepared from the P3HT nanofibers fabricated during the dry season or the humid season.

**Figure 3.2.** J-V curves obtained from the electrospun OPV device and bilayer
cells fabricated during the dry season or the humid season.

**Figure 3.3.** SEM micrographs of the P3HT@PEO composite fibers (a and b) and of the virgin P3HT fibers (c and d). Fibers were electrospun in the dry season (a and c) or in the humid season (b and d).

**Figure 3.4.** PL properties of the virgin P3HT nanofibers and the composite films composed of PC_{60}BM and virgin P3HT nanofibers.

**Figure 3.5.** SEM images of electrospun P3HT@PEO composite fibers prepared at (a) 20%, (b) 30%, (c) 40%, and (d) 50%.

**Figure 3.6.** SEM images of electrospun P3HT fibers prepared at (a) 20%, (b) 30%, (c) 40%, and (d) 50%.

**Figure 3.7.** Variations in the diameters of the electrospun fibers and beads as a function of the RH.

**Figure 3.8.** Variations in the solvent evaporation rate under different RH conditions.

**Figure 3.9.** Schematic of electrospinning process under low (left) and high (right) RH.

**Figure 3.10.** SEM image of electrospin PEO fibers prepared from 0.5 wt% spinning dope solution at 50% RH.

**Figure 3.11.** SEM micrographs of the P3HT@PEO composite fibers prepared from spinning dope solutions having a (a) 0.35 wt%, (b) 0.3 wt%, or (c) 0.25 wt%
PEO concentrations, spun under a heater system.

**Figure 3.12.** Schematic of electrospinning process under a heater system.

**Figure 3.13.** SEM micrographs of the P3HT@PEO composite fibers prepared from spinning dope solutions having a (a) 0.3 wt%, or (c) 0.25 wt% PEO concentrations at 20% RH.

**Figure 3.14.** J-V curves obtained from the electrospun OPV devices prepared from the P3HT nanofibers prepared during the dry season or with heating during the humid season.

**Figure 4.1.** Schematic diagram showing the preparation of a nanofibrous OPV device.

**Figure 4.2.** SEM micrographs of the electrospun PCDTBT@PEO nanofibers prepared from solutions containing various concentrations of the polar solvents and PEO. The concentrations of PEO were 0.3 wt% (a, d, g), 0.4 wt% (b, e, h), and 0.5 wt% (c, f, i). The chloroform:polar solvent ratios were 10:1 (w/w) (a, b, c), 8:1 (d, e, f), and 6:1 (g, h, i).

**Figure 4.3.** The viscosities of the spinning dope solutions.

**Figure 4.4.** (a) Electrospun PCDTBT@PEO composite nanofibers with lengths greater than one centimeter. (b) SEM image, (c) optical image, and (d) fluorescence micrographs of the electrospun PCDTBT@PEO composite
nanofibers. (e) TEM micrographs of the electrospun virgin PCDTBT nanofibers under low magnification or (f) high magnification.

**Figure 4.5.** FT-IR spectra of electrospun PEO fibers, PCDTBT@PEO composite fibers and PCDTBT virgin fibers.

**Figure 4.6.** TEM micrographs of the virgin PCDTBT nanofibers with a diameter of (a) 50 nm, and SEM micrographs of virgin PCDTBT nanofibers with diameters of (b) 120 nm, and (c) 200 nm.

**Figure 4.7.** Thermogravimetric thermograms of the samples under isothermal treatment at 370°C.

**Figure 4.8.** (a) UV-Visible absorption spectra of the PCDTBT nanofibers with different diameters in comparison with the spectrum from a PCDTBT film. (b) Spectra magnified over the range 540–610 nm.

**Figure 4.9.** TEM micrographs of (a) PCDTBT film and (b) virgin PCDTBT nanofibers. The insets show the SAED patterns of the samples.

**Figure 4.10.** N₂ adsorption isotherms (at 77 K) for the PCDTBT powders and fibers.

**Figure 4.11.** (a) The PL properties of virgin PCDTBT nanofibers with various diameters: PCDTBT nanofibers only (20 nm); active layer composed of PCDTBT nanofibers and PC₇₀BM (200 nm, 120 nm, 50 nm, 20 nm). (b) J-V
curves for the OPV devices composed of PCDTBT nanofibers with various diameters.

**Figure 4.12.** Current density–voltage characteristics of an air-processed BHJ OPV device without an interlayer (black line), with a LiF interlayer (red line), and with a TiOₓ interlayer (blue line).

**Figure 4.13.** AFM images (2 µm x 2 µm) of the (a) BHJ, (b) pseudo-bilayer, and (c) nanofibrous active layers composed of PCDTBT:PC₇₀BM.

**Figure 4.14.** (a) J-V curves and (b) IPCE spectra of the devices prepared using the PCDTBT:PC₇₀BM BHJ, pseudo-bilayer, and nanofibrous structures.

**Figure 4.15.** Device performance variation on the exposure time in ambient air.

**Figure 4.16.** Calculated photocurrent density–voltage curves of the devices prepared using the PCDTBT:PC₇₀BM BHJ, pseudo-bilayer, and nanofibrous structures.

**Figure 4.17.** Dark J¹/²-V characteristics for the SCLC hole-only devices prepared using the PCDTBT:PC₇₀BM BHJ, pseudo-bilayer, and nanofibrous structures.

**Figure 4.18.** Cross-sectional TEM defocused (~ -10µm defocused) phase contrast images of (a) BHJ device (b) pseudo-bilayer device and (c) nanofibrous device (Scale bar: 50 nm). (d) Cross-sectional TEM bright image
of BHJ device.

**Figure 5.1.** J-V curves of P3HT:PC$_{60}$BM devices treated by solvents.

**Figure 5.2.** SEM micrographs of the (a) GO(S), (b) GO(M), and (c) GO(L).

**Figure 5.3.** Images of (a) GO(S), GO(M), and GO(L) dispersed in IPA after vigorous stirring and (b) after stirring for 1 day.

**Figure 5.4.** (a) Stability of P3HT:PC$_{60}$BM cell under an ambient condition and (b) comparison of the cell performance under an ambient condition for cells without encapsulation and with GO and rGO encapsulation.

**Figure 5.5.** Images of (a) GO(L) and GO(L, sonic) dispersed in IPA and (b) 1 month after dispersion. SEM images of (c) the GO(L) and (d) GO(L, sonic) samples.

**Figure 5.6.** Stability of the cell performance under an ambient condition for cells without encapsulation and with rGO(L) films.

**Figure 5.7.** AFM images of (a) the GO(L) and (b) GO(L, sonic) samples.

**Figure 5.8.** XRD patterns of GO(L) and GO(L, sonic) samples.

**Figure 5.9.** Images of (a) GO film on PEN substrates, (b) after dipping in NaBH$_4$ solution for 2 hours at 80 °C, and (c) after thermal annealing at 200 °C.

**Figure 5.10.** Picture (a, b, c) and optical microscopy image (d, e, f) of the (a, d) GO(L, sonic), (b, e) rGO(L, sonic)_10C and (c, f) rGO(L, sonic)_01C samples.
Figure 5.11. AFM images of (a) GO(L, sonic), rGO(L, sonic)_10C and (b) rGO(L, sonic)_01C.

Figure 5.12. SAXS curves of the products.

Figure 5.13. C1s XPS spectra of the GO and rGO films.

Figure 5.14. Efficiency variation of PCDTBT:PC70BM inverted OPV devices encapsulated by PEN/rGO film stored at (a) ambient air and (b) 100% relative humidity.

Figure 5.15. Image of a flexible OPV device based on the flexible TCF and gas barrier film.

Figure 5.16. J-V curves of the flexible devices.

Figure 5.17. Normalized photovoltaic parameter as a function of the number of bending cycles.
Part I

Basic research for organic photovoltaic devices
Chapter 1. Introduction

1.1 General introduction to photovoltaic devices

1.1.1 Overview of photovoltaic devices

During the last few decades, energy and environmental problems have become globally critical issues due to the exhaustion of fossil fuels and climate change. To replace fossil fuels and prevent the emission of carbon dioxide, renewable energy resources are widely studied at present. Among the various renewable energy sources, solar energy is regarded as the most feasible next-generation energy source, as solar energy can be changed to electricity without territory restrictions and because the energy generation capacity of this method is ample enough to supply the total energy consumption requirements on Earth. However, the portion of solar energy in energy production is very low at present1 (see Figure 1.1) because the cost of electrical energy generated by solar cells is much higher than that of other energy sources2 such as fossil fuels, nuclear energy and wind energy (see Figure 1.2) owing to the high cost of silicon wafers and the high-temperature vacuum process required. Solar cells have other issues to overcome before they can replace conventional power plants, including the low throughput of the fabrication method. Moreover, silicon solar cells are inappropriate for the flexible devices due to the brittleness of the material, which stands in contrast to the development trends of electronic devices.
Figure 1.1. Estimation of (a) primary energy consumption and (b) renewable energy consumption
Figure 1.2. Generation cost for electricity from various energy sources
1.1.2 Demand for generation photovoltaic devices

Therefore, it is imperative to develop the next generation of photovoltaic devices to overcome the abovementioned fundamental problems of silicon-based solar cells. Considering the issues associated with current photovoltaic devices, the first condition for next-generation photovoltaic devices is a lower generation cost of electricity. Low-cost photovoltaic devices can lead to the utilization of clean and abundant solar energy.

To reduce the price of photovoltaic devices, the expansive silicon wafer should first be replaced with another material. Second, the fabrication technique should be vacuum-free and should involve low-temperature processing instead of the conventional deposition technique. Solution-processing can be an alternative to the conventional deposition technique, as it decreases the fabrication cost and energy payback time. The second condition for next-generation photovoltaic devices is high throughput. Solution-processing provides high throughput if the roll-to-roll printing method is used.

In other words, solution-processing not only solves the cost problem, but it increases the throughput as well.

Third, flexibility of the devices is essential for next-generation electronic applications. Flexible devices are divided into four stages: unbreakable, bendable, rollable, and foldable devices. Higher flexibility is required to achieve a higher stage of flexible device. To prepared flexible devices, glass substrates as well as silicon wafers should be replaced with other flexible materials. In addition, the layers on the device should consist of flexible materials.

The fourth condition is high stability and a long lifetime of the devices. Because long lifetimes of devices decrease the unit cost of electricity, the unit cost of a photovoltaic device with a short lifetime will increase even if the materials are inexpensive and the processing costs are low. If the lifetimes of photovoltaic devices are shorter than the
energy payback time, it is recommended not to fabricate the devices.

The last condition for next-generation photovoltaic devices is high performance. Silicon-based photovoltaic devices exhibit 25% power conversion efficiency on the laboratory scale and around 15% efficiency in commercial products. The next generation of photovoltaic devices should satisfy the four conditions mentioned above and also show efficiency as high as that of silicon photovoltaic devices.

To satisfy these conditions, materials that can be solution-processed and that are flexible, highly stable in ambient air, and highly efficient should be investigated. It is clear that new materials different from conventional silicon-related materials are required.

1.1.3 Next-generation photovoltaic devices: sp²-carbon-based organic photovoltaic devices

As a solution to the above issues, carbon-based electronics are preferred over silicon-based electronics due to their solution-processable nature, low cost, and flexibility. In general, carbon-based materials are capable of solution processing, which greatly reduces processing costs and allows high throughput through continuous processing.

The cost competitiveness of carbon-based materials is made possible by the formation of thin films even without expensive substrates like silicon wafers. Unlike high-crystalline inorganic matter, they are highly flexible and thus suitable for use in next-generation electronic devices. These carbon-based electronics can be largely divided into two categories: carbon nanomaterials and conjugated polymers. The former consists of zero-dimensional fullerenes, one-dimensional (1-D) carbon nanotubes (CNTs), and two-dimensional graphene; while the latter contains C-C bonds achieved by sp² hybridization (see Figure 1.3). Both categories exhibit conductive
characteristics since their C-C bonds are in sp² configuration. Carbon nanomaterials and conjugated polymers can be used to substitute solar cell components, so as to create a next-generation device that overcomes the limitations of existing silicon solar cells.
Figure 1.3. The carbon atoms form 0D fullerene, 1D CNT, 2D graphene, and 3D graphite structures.
Organic photovoltaic (OPV) cells are alternative solar cells in which a conjugated polymer-based layer replaces the active layer, which is responsible for absorbing light to generate electric charge. OPV has developed rapidly over the past 20 years, and with an efficiency exceeding 10%, it is nearing the performance of silicon-based thin film solar cells. Due to the high potential for roll-to-roll processing and flexibility resulting from conjugated polymer characteristics, OPV is within close proximity of the ideal next-generation solar cell.

The main focus of recent OPV studies is PCE enhancement through the synthesis of new conjugated polymer. The rapid increase in efficiency is astonishing, but more stages are involved in synthesis as the structure of polymers grow complex, and this is accompanied by a loss in cost competitiveness. Also, there are many issues yet to be resolved regarding flexibility and lifespan, which have been less extensively studied. This research examines theories on sp²-carbon materials including conjugated polymer and conducts a fundamental study on OPV structure and operation principles. Directions for further studies will be determined based on the findings.

1.2 Theoretical consideration for the sp²-carbon-based photovoltaic devices

1.2.1 Review of carbon-based electronic materials

1.2.1.1 Carbon nanomaterials
Carbon nanomaterials have attracted a great deal of interest in electronic research areas due to their remarkable electrical properties. Possible applications of carbon nanomaterials in electronic devices include the field emission display, the transparent
conducting electrode, and the solar cell. Carbon nanomaterials are divided into zero-dimensional fullerene, 1-D CNT, and two-dimensional graphene. These carbon nanomaterials have not only different shapes but also different physical characteristics. Due to their distinct physical and structural features, carbon nanomaterials are used in different applications. Moreover, the tunable chemical and physical characteristics of carbon nanomaterials are useful when preparing tailor-fitted materials.

Fullerene is composed of 60 carbon atoms that form a shape resembling a soccer ball. Despite the low electrical performance compared to other carbon nanomaterials, the solubility of the material is high enough to be solution-processed. In addition, the homogeneity of the materials is much higher than that of CNTs and graphene, leading to high reliability in electronic devices. Because fullerene is a semiconducting material with a bandgap, it is appropriate for use in semiconducting devices, including OPV devices. Indeed, the most well-known materials used in the electron acceptors of OPV devices are fullerene derivative materials that have functional groups on the surface of the fullerenes that can be dissolved in organic solvents. The high solubility and electron-accepting performance of fullerene derivatives make them the best electron acceptors in OPV devices. Among fullerene derivatives, ([6,6]-phenyl-C_{61}-butyric-acid-methyl-ester) PC_{61}BM is the best-known fullerene derivative in research related to the development of OPV devices. Currently, new derivatives are being introduced to increase the power conversion efficiency.9
Figure 1.4. Molecular structure of fullerenes and their derivatives.°
CNT is a 1-D carbon nanomaterial with a very high aspect ratio. It is a desirable material for use in electronic devices due to its high electrical properties and good structural characteristics.\textsuperscript{11} Surface modification of CNTs improves their dispersibility and enables solution-processing. In addition, CNTs are appropriate materials for next-generation flexible devices due to the flexibility of CNT films.

The formation of CNT can be assumed by the rolling of a graphene sheet into a cylinder. The rolling direction of the graphene sheet is described by the chiral vector, defined by the equation \( \mathbf{C} = n \mathbf{a}_1 + m \mathbf{a}_2 \), where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) denote the graphene lattice basis and the indices \((n,m)\) are the number of steps along the zig-zag carbon bonds (see Figure 1.5).\textsuperscript{12} The chirality determines not only the rolling direction but also the electrical properties CNTs. When \( n-m=3p \) (\( p \) is an integer), the CNT is metallic, and when \( n-m\neq3p \), the CNT is semiconducting. Considering that control of the chirality is challenging, this inhomogeneity of CNTs is a hindrance when creating workable devices. Specifically, metallic materials incorporated in the active layer of OPV devices can act as a recombination center, leading to low efficiency of the devices. Instead, CNTs can be used as a transparent conducting film or as a charge transport layer.\textsuperscript{13} Further research on the control of the chirality or the separation of CNTs with different levels of chirality will lead to the incorporation of CNTs in the active layers.
Figure 1.5. Chiral vector on unrolled graphene sheet. The vectors OA and OB are the chiral and translational vectors, respectively.\textsuperscript{12}
Figure 1.6. Molecular structures of CNTs and functionalized CNTs.
Graphene is a two-dimensional monolayer of atomic carbon as an exfoliated carbon layer from graphite. Because the thickness of graphene is very thin, it has a very high aspect ratio. Graphene is one of the most important candidates for flexible devices due to its superior electrical properties and good flexibility.\textsuperscript{14} A few synthesis methods have been suggested for the preparation of graphenes.\textsuperscript{15} Interestingly, the physical properties of graphene are different depending on the synthesis method. The first method is mechanical exfoliation from graphite. Scotch tape is used to exfoliate one graphene layer from graphite mechanically. Graphene prepared in this way shows good properties and is appropriate for fundamental studies, but the throughput is very low. The second method is CVD synthesis, which is similar to the conventional thin-film fabrication method. Recently, large-area graphene film produced by the CVD method exhibited high performance. However, the fabrication cost and uniform growth remain challenges. The third method is to realize chemically exfoliated graphene layers from graphite by oxidation. Graphite oxide can be well dispersed in water as a single layer due to the large amount of oxidative functional groups.\textsuperscript{16} Graphite oxide is subsequently reduced by a reduction agent, resulting in reduced graphene oxide.\textsuperscript{17} The chemical exfoliation method is an appropriate method for large-scale production and is feasible for use with solution-processing. However, the physical properties are lower than that of graphene fabricated from the CVD method. Instead, the large amount of functional groups on the surface of graphene oxide enables secondary functionalization and chemical tuning, leading to the preparation of tailor-fitted materials.
Figure 1.7. Preparation method of reduced graphene oxide.
A theoretical basis must be first established because carbon nanomaterials can exist in various forms and exhibit very different characteristics. The selected carbon nanomaterials should match the characteristics of materials in each part or be tuned as required.

1.2.1.2 Conjugated polymers
Conjugated polymer is a polymer that allows electricity to pass through it via a π-conjugated system made possible by means of alternating single and double bonds. Unlike general polymers, it is capable of solution processing and flexible enough to be used in flexible devices. Conjugated polymer-based solar cells, with their high absorbency, efficiently absorb light even at a thickness of 100 nm. This is highly beneficial in reducing the amount of materials needed. Although less conductive compared to inorganic materials, they are able to power devices as OPV operates at thin thickness when used as active material for solar cells.

Conjugated polymer began in the form of materials like polyacetylene in the early days, and moved onto poly (p-phenylene vinylene) (PPV) and polythiophene during the 1990s to early 2000s. From the late 2000s, it was synthesized with various copolymers. Looking at the performance of major conjugated polymers, PPV has an efficiency of 2~3%, and P3HT, a derivative of polythiophene, has an efficiency of 4~5%. With poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) recording a high efficiency of 5.5% and poly[N-9′-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) of 6.1% in the late 2000s, research began on the synthesis of new and high-efficiency conjugated polymers. Since 2010, many polymers have recorded efficiency rates higher than 7%, and the single cell poly(4,8-bis[(2-
ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl} {3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7) with 9.2% efficiency\(^{24}\) is now widely used. Thus, the efficiency in OPV greatly depends on the choice of conjugated polymer.
Figure 1.8. Molecular structure of representative conjugated polymers.¹⁰
One of the disadvantages of conjugated polymer is that it is easily oxidized when exposed to air, which is the reason for the short lifespan of organic devices. Oxidization occurs when oxidizing agents such as moisture or oxygen react with conjugated polymer in a photochemical reaction, causing it to lose photochemical/electrical characteristics and leading to a loss of efficiency. The lifespan of active materials in organic light-emitting diodes (OLEDs), used in mobile phones, also determines the lifespan of the device. OLEDs have been criticized for having a shorter lifespan compared to liquid-crystal displays (LCDs). All processes must be carried out under atmosphere to prevent oxidization, and this involves higher costs.

1.2.2 Structure of the OPV devices

In order to take on the characteristics of next-generation devices, there should first be a theoretical investigation of OPV structure and the materials constituting each part. OPV is usually structured as electrode/active layer/electrode, and an encapsulation layer is added to overcome the problem of short lifespan mentioned above. A few layers are added to the basic structure to improve efficiency, and the most commonly used structure these days is glass substrate/transparent electrode/hole transport layer (HTL)/active layer/hole blocking layer (HBL)/metal electrode/glass substrate. The following is a review of the role and material of each structure.
Figure 1.9. Device structure of OPV devices.
1.2.2.1 Transparent electrode

For solar cells to work, light must enter through the active layer, which means that one electrode has to be transparent. The same applies to OLEDs and LCDs, and indium tin oxide (ITO) is the most common material used in transparent electrodes. ITO is adequate as the anode of solar cells due to its high transmissivity, low sheet resistance, and a work function of 4.7~5.0 eV. Because of its highly reliable performance, ITO has been used for most transparent electrodes in recent devices. However, it is expensive and brittle. The depletion of indium makes ITO costly, and there may be a decline in performance during the bending test. Eventually, alternative materials are required for OPV.

Transparent electrodes are being actively studied independently of OPV, and alternative materials include graphene, CNT, silver nanowire, conjugated polymer, and patterned metal. The advantages and disadvantages of each material are summarized in Table 1.1.
Figure 1.10. AFM image of (a) CNTs based transparent conducting electrode and (b) graphene film. (d) SEM image of silver nanowires based electrode.26

Table 1.1. List of various materials for transparent conducting films27

<table>
<thead>
<tr>
<th>Material</th>
<th>Transistor properties</th>
<th>Conductivity [for TE]</th>
<th>Flexibility</th>
<th>Transparency</th>
<th>Cost</th>
<th>Processability</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
<td>Average</td>
<td>Excellent</td>
</tr>
<tr>
<td>Organics</td>
<td>Average</td>
<td>Average</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Average</td>
</tr>
<tr>
<td>Inorganics</td>
<td>Excellent</td>
<td>N/A</td>
<td>Good</td>
<td>Poor</td>
<td>average</td>
<td>Average</td>
<td>Excellent</td>
</tr>
<tr>
<td>Metal oxides</td>
<td>Good</td>
<td>Excellent</td>
<td>Good</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Metal NWs</td>
<td>N/A</td>
<td>Excellent</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
<td>Average</td>
</tr>
<tr>
<td>Graphene</td>
<td>Poor</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Good</td>
<td>Average</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

23
1.2.2.2 Hole transport layer

The active layer was placed right above ITO in early OPVs, but an additional layer for hole transmission between the active layer and ITO offers many advantages such as the formation of ohmic contact, ease of spin coating, and reduction of surface roughness. To achieve improved performance, the HTM layer is included in most cells. The HTM layer has similar physical properties to the transparent electrode layer since it has to maintain high transmissivity, conductivity, adequate work function, and valence band offset. Current flow follows the direction of the film surface for the transparent electrode layer, but passes through the film and travels for a shorter distance in the case of the HTM layer, enabling the use of materials that are relatively weaker in conductivity. This layer is distinguished from the transparent electrode layer in the formation of ohmic contact with the active layer and compatibility.

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is the most widely used material for the HTM layer. As a conjugated polymer dispersed in water, PEDOT:PSS easily forms thin films through spin coating, and satisfies the conditions of the HTM layer in terms of transmissivity, conductivity, and work function. Suggested alternatives include conjugated polymers like polyaniline-based materials and inorganic materials such as MoO$_3$, NiO, and V$_2$O$_5$, but PEDOT:PSS still remains the most widely spread material.

1.2.2.3 Active layer

1.2.2.3.1 Formation of excitons in a polymer

The structure of the active layer in an OPV cell is somewhat different from that of a silicon solar cell at present, although these concepts were similar at an early stage. In 1970, both silicon solar cells and organic solar cells had the same structure, but the
efficiency of the organic solar cell was very low due to the low physical properties of the organic materials used. To achieve high efficiency of an OPV device, a novel structure that was not used in conventional silicon solar cells was introduced. As a result, the operation physics and requirements of the material become somewhat different from those of a silicon solar cell. The most significant reason for the development of a new structure is the low dielectric constant of the organic material. Here, the consequences of the low dielectric constant and the development of new structures will be reviewed.

Both silicon and organic semiconductors absorb photons and transport electric charges to each electrode, but the charge generation processes are somewhat different due to the low dielectric constant of the organic semiconductor. When an electron in silicon absorbs a photon, the electron in the valence band is excited to the conduction band and the energy state of the electron becomes higher. Due to the Coulomb force between the excited electron and hole in the valance band, the electron and hole act as a pair. The Coulomb force is given as follows:

\[ F = -\frac{q_1 q_2}{4\pi \varepsilon_0 r^2} \]

The electric energy between the electron and the hole (~10meV) in silicon is lower than the thermal energy (~25meV) at room temperature, therefore, they are separated spontaneously. These dissociated electron and hole pairs move to each electrode via an internal electric field. In the case of organic materials, the Coulomb force between the electron and the hole is much stronger than the attraction force in silicon, as the dielectric constant of the organic material is lower than that of silicon. Therefore, the electron-hole pair is not dissociated spontaneously; this is referred to as an exciton. Given that the exciton is recombined in a few nanoseconds, electric energy cannot be
generated in an OPV device. This is the reason for the low efficiency of OPV cells, and spontaneous dissolution is an important issue pertaining to OPV operations.

1.2.2.3.2 Heterojunction structure
Tang solved this problem by introducing a bilayer structure which was composed of an electron donor layer and an electron acceptor layer. The acceptor has a lower LUMO level compared to that of the electron donor, and the electronic energy level difference induced exciton dissociation. Copper phthalocyanine (CuPc) was used as the electron donor and perylene tetracarboxylic derivative (PV) was used as the electron acceptor in this system, as the difference between the LUMO levels of CuPc and PV was greater than the exciton binding energy. Therefore, the excited electrons were able to move from the LUMO level of CuPc to the LUMO level of PV. This phenomenon is known as photoinduced charge transfer (PICT), and it takes only 45 fs, which is much faster than luminescence decay. The power conversion efficiency of the solar cell was nearly 1%, which was a noticeable improvement compared to previous organic solar cells.

1.2.2.3.3 Limited exciton diffusion length in a polymer
Although the bilayer structure substantiated exciton dissociation, this structure is known for another problem. Because the exciton diffusion length is short (5~15 nm), only excitons generated near the interface can be dissociated while other excitons absorbed in an area apart from the interface cannot be dissociated. Decreasing the thickness of the absorption layer enables almost 100% exciton dissociation, but the absorption of photons becomes a problem in this case because a thickness of at least 50 nm is required for the absorption of photons using 10⁵ cm⁻¹ absorption coefficient materials. Therefore, maintaining the thickness of the absorption layer and exciton
diffusion to the interface should be realized at the same time. This contradictory problem remained unsolved until 1995.  

1.2.2.3.4 Bulk heterojunction structure

The effective exciton dissociation and absorption of photons was realized using a bulk heterojunction (BHJ) structure in 1995.  

The distance from the absorption spot to the interface of the donor and acceptor was remarkably decreased by the inter-penetration of the electron donor and acceptor. Furthermore, this structure was formed with a very simple process in which a BHJ-structured OPV cell was fabricated by the spin-casting of a solution that contained donor and acceptor materials. Due to the advantages of the BHJ structure, most OPV devices that show high efficiency have a BHJ structure. Because the mixture state of the donor and acceptor determines the exciton dissociation and charge transportation, control of the BHJ structure has been a main research topic over the last 15 years.

1.2.2.4 Cathode

As for the cathode, a metal electrode with a low function is typically used. The most commonly used material is aluminum, with a work function of 4.3 eV, which responds well to the work function of PC_{60}BM. Higher efficiency can be obtained by adding calcium or other metals having lower values for work function before aluminum. While PEDOT:PSS acts as the buffer layer on the anode side of most OPVs, the cathode-side buffer layer plays more diverse roles and may not always be present. TiO_x, acting as HBL, is one of the most widely known buffer layers of cathodes. Similar to the HTM layer, it demands high transmissivity and conductivity. An optimal band structure is required to permit the flow of electricity while blocking holes.
Common HBL materials are TiO$_x$, ZnO, and BCP, and materials like LiF are used as a buffer layer forming dipoles at the interface. In recent studies, the Ca/Al combination has been frequently used.

1.2.2.5 Encapsulation layer
The encapsulation layer not been covered as much in OPV studies, but it is necessary for the use of devices in an ambient atmosphere.$^{36}$ This layer blocks out moisture and oxygen so that oxidizing agents do not enter the active layer. Recent studies have found that moisture is one of the major causes for shorter lifespan in organic electronic devices. As such, the most important role of the encapsulation layer is to prevent the expansion of moisture. Since expansion occurs through upper and lower layers, both parts have to be encapsulated. The transparent electrode layer is less problematic thanks to the low moisture transmissivity of the glass substrate. The cathode side, however, is exposed to ambient conditions and allows large amounts of moisture to enter. To prevent the infiltration of moisture, the glass can be protected by epoxy and other adhesives.

1.3 State-of-the-art works on OPV devices

1.3.1 High-performance devices
Over the past decade, substantial progress has been made in the design and synthesis of new conjugated polymers and new electron acceptors, as well as morphology control and characterization. As a result, high efficiencies of 9.2% for single-junction devices$^{24}$ and 11% for tandem devices$^5$ have been realized.
1.3.1.1 Synthesis of a new conjugated polymer

P3HT is one of the most widely used materials because of the merits of easy synthesis, a high mobility, and good processability. However, P3HT has some demerits to be used in OPV devices such as large bandgap and high HOMO level. The large bandgap of the P3HT leads to insufficient absorption at the near infrared region. The high HOMO level induces low open-circuit voltages of OPV devices. Therefore, control of the bandgap and HOMO level has been an important issue in OPV studies. Several material designs have been proposed to synthesize the new materials. For examples, synthesis of co-polymer composed of electron-rich donor and electron deficient acceptors or attachment of the electron withdrawing groups have been known to decrease the bandgap of conjugated polymers. Based on these approaches, many conjugated polymers have been designed and synthesized recently.

1.3.1.2 Synthesis of a new acceptor

Electron acceptors play an equally important role as the electron donors in OPV devices. In 1995, Heeger et al. suggested the BHJ structure for the OPV devices incorporating PC_{60}BM as an electron acceptor blended with conjugated polymer. Since then, fullerene derivatives are widely adopted as an electron acceptor material in solution processed OPV devices. Indeed, OPV devices capable of more than 5% efficiency adopt fullerene derivatives as an electron acceptor. Specifically, the incorporation of PC_{70}BM and a low-bandgap polymer shows high performance levels due to the high absorption coefficient in the visible light range of PC_{70}BM. Recently, the increase in the open-circuit voltage has become an issue in efforts to enhance the power conversion efficiency. Many research groups have concentrated on the synthesis of new conjugated polymers with a low LUMO level to achieve a high
open-circuit voltage. In contrast, other attempts have been made to increase the open-circuit voltage by tuning the LUMO level of the electron acceptor. Indeed, 6.5% efficiency without the synthesis of a new conjugated polymer was achieved with the ICBA (indene-C_{60} bisadduct).\textsuperscript{38} The incorporation of P3HT and ICBA increased the open-circuit voltage by nearly 40% compared to the conventional incorporation of P3HT and PC_{60}BM. Because the synthesis of a new conjugated polymer is complicated and time-consuming work, the tuning of fullerene derivatives to enhance the open-circuit voltage will be a critical issue for next-generation OPV devices.

1.3.1.3 Control of the morphology

Although the BHJ structure solved the exciton dissociation problem in a bilayer structure, charge transportation to the electrode became another problem. Because the active layer is in a random mixture state, connections between materials are not completely formed. The electric charges that remain in the active layer would recombine each other, implying that there is much room for improvement of the short-circuit current. Furthermore, the morphology also affects the charge mobility, which is a main factor determining the short-circuit current. Indeed, many research groups have focused on controlling the morphology using various methods to form a transport pathway, and the power conversion efficiency has been increased using the same materials. For example, a P3HT-PC_{60}BM-based solar cell showed less than 3% efficiency initially, but it shows efficiency of approximately 5% currently. Proper morphology control influences the performance of OPV devices significantly.

1.3.1.3.1 Conventional method to control the morphology of the active layer

Thermal annealing is a widely used means of improving the short-circuit current.\textsuperscript{39,40}
Annealing at a high temperature induces domain growth of the materials, and a charge transport pathway is easily formed due to the large domain. Figure 1.11 shows the morphological differences after annealing P3HT/PC_{60}BM film. The formation of a charge transportation pathway by phase separation is easily confirmed in the figure. Therefore, the short-circuit current and PCE difference with different annealing temperatures and times both changed. In order to achieve optimized domain growth for exciton dissociation and charge transport, an appropriate annealing temperature was investigated several times, and annealing at 150 °C was regarded as the best condition for the combination of P3HT and PC_{60}BM. The solvent and evaporation rate change the morphology remarkably during the spin-coating process. Shaheen et al. used chlorobenzene instead of toluene; their chlorobenzene-cast OPV had a smooth surface and showed high power conversion efficiency levels. Hummelen et al. showed that xylene creates too large a domain to harvest excitons, and the smallest domain which increases charge recombinations was observed with o-dichlorobenzene. Chlorobenzene was shown to be the best solvent to obtain an optimum morphology, which is why most OPVs are currently prepared using chlorobenzene. Without changing the solvents, the efficiency also increases by adjusting the evaporation time of the solvent. The hole mobility and electron mobility of slowly grown film are similar (See Figure 1.12), which is important for improving the power conversion efficiency because an unbalanced charge carrier mobility causes the accumulation of the charge carriers, which generate an electric field against the built-in electric field.
Figure 1.11. TEM images of a P3HT:PC$_{60}$BM film (a) before and (b) after thermal annealing.\textsuperscript{43}
Figure 1.12. Influence of film growth rate on the carrier mobility.\textsuperscript{42}
1.3.1.3.2 **Rational morphology control by 1D conjugated polymers**

The efficiency of OPV devices has been improved by the abovementioned materials and morphological control methods. Considering that the theoretical limitation of the short-circuit current of P3HT is 15.2 mA/cm², approximately 80% theoretical efficiency is achieved in present based on the P3HT-PC₆₀BM active layer.⁴⁴ However, the random morphology of the BHJ structure generates isolated areas, thus decreasing the overall current. Furthermore, the BHJ structure is inappropriate for inorganic acceptors according to photoluminescence testing due to the aggregation of the surfactant on the nanoparticles.⁴⁵ In this situation, 1-D materials can be a feasible solution to control the morphology. Instead of a random mixture in the BHJ structure, 1-D materials with controlled widths or diameters readily form percolated pathways. An ordered heterojunction, as depicted in Figure 1.13(d), is one type of the 1-D structure that has a continuous phase of the electron donor and acceptor. To fabricate 1-D materials, template-based and self-assembly methods are suggested for the formation of an ordered structure.
Figure 1.13. Scheme of (a) single layer structure (b) bilayer structure (c) BHJ structure and (d) ordered heterojunction structure.
An aluminum anodized oxide (AAO) template is a strong candidate for realizing an ordered structure due to its shape (Figure 1.14). The well-ordered pore array of AAO has a high aspect ratio, and its diameter and alignment can be easily tuned. Numerous metal, metal-oxide and polymer nanorods are fabricated with AAO templates. OPVs with TiO$_2$, CdTe, and CdS nanorods have been investigated, and ZnO or CdSe nanorods are expected to be used because these materials show better performance as electron acceptors for OPVs. TiO$_2$ nanorods were used as DSSCs as well as OPV devices. However, in-depth study is still required because the efficiencies of the cells are lower than those of conventional solar cells.
Figure 1.14. AAO template-based nanotechnology, (a) after the infiltration of TiO₂, (b) cross-sectional image of (a), (c) after the removal of AAO, and (d) cross-sectional image of (c).⁴⁶
OPVs with ordered structures are composed of an inorganic acceptor fabricated with an AAO template and a spin-coated conjugated polymer. Considering that the conjugated polymer is an absorption material and that its diameter should be smaller than the exciton diffusion length, the ordered structured OPV should be composed of a conjugated polymer based on an AAO template and spin-coated inorganic materials, which is opposite from the method above (Figure 1.15).\textsuperscript{51} Another advantage of this conjugated polymer nanorod is that it has higher mobility.\textsuperscript{52} Considering that the low mobility of a conjugated polymer is one of the main problems preventing their development in relation to OPVs, conjugated nanorods can be a solution.
Figure 1.15. (a) Scheme of P3HT nanorod/fullerene structure OPV device. SEM images of (b) top and (c) side views of AAO template and (d) P3HT nanorods.\textsuperscript{51}
Another approach to form a 1-D conjugated polymer is the self-assembly of conjugated polymer into fibers or wires.\textsuperscript{53} It is known that the self-assembly of a conjugated polymer can be induced in a marginal solvent\textsuperscript{53} or by adding a poor solvent.\textsuperscript{54} In 2007, Guillerez et al. reported that self-assembled P3HT nanowires exhibit a PCE rate of 3.6% without annealing.\textsuperscript{53} In comparison, a conventional BHJ-structured OPV device prepared from amorphous P3HT and PC\textsubscript{60}BM without thermal annealing showed a PCE rate of 0.65%. The authors prepared the P3HT nanowires in p-xylene, which is a marginal solvent for P3HT. P3HT was initially oversaturated in the marginal solvent and self-assembled into nanowire while cooling. The typical dimensions of the fibers were 0.5–5 \( \mu \)m in length, 30–50 nm in width and 5–15 nm in thickness (\textbf{Figure 1.16}).
Figure 1.16. (a) SEM and (b) AFM images of P3HT nanowire obtained by self-assembly method.
A second method which can be used to create conjugated polymer nanowires involves an addition of a poor solvent for conjugated polymers. The self-assembly behavior of the conjugated polymer is similar to that in the marginal solvent method. Conjugated polymers are dissolved in a good solvent initially, after which poor solvents are added. The polymers are aggregated into the nanowires induced by the poor solvent. These 1-D nanowires have not only a continuous morphology but also high crystallinity. Because the high crystallinity induces high mobility of the materials, 1-D materials have an advantage for charge transport.

1.3.2 Long-lifetime devices
1.3.2.1 Encapsulation design
The simplest example of encapsulation on a laboratory scale involves the use of glass, but the thick thickness and brittleness of glass prevent the application in flexible devices. High-performance gas barrier thin films have been studied recently due to the development of organic electronic devices. These thin films were prepared by a vacuum deposition method. Typical materials for the encapsulation film are inorganic materials such as Si, SiN, or Al2O3, and a multilayer of inorganic materials or inorganic/organic hybrids is used to obtain high performance. An encapsulation film composed of a multilayer material showed a water vapor transmission rate (WVTR) value of 10^{-4} g/m^2 day, which is appropriate for use in OPV devices.

1.3.2.2 Inverted solar cell
PEDOT:PSS is an essential material for improving OPV devices via the formation of an ohmic contact between the conjugated polymer and ITO. However, it is unfavorable for maintaining the performance of an OPV device due to its material properties.
PEDOT:PSS is dispersed in a very highly acidic aqueous solution, leading to the corrosion of the ITO. In addition, the performance of PEDOT:PSS is degraded in an ambient atmosphere due to the hygroscopic nature of PSS. Aluminum, which is used as a metal electrode, is also easily oxidized and thus degrades the performance of the active layer by the diffusion of aluminum into the active layer. Therefore, the stability of the OPV device can be significantly enhanced by replacing the PEDOT:PSS and aluminum with other materials.\(^2\)

In a normal structure of an OPV device, electrons are transported to an aluminum electrode and holes are transported to an ITO electrode. A metal with a low work function is necessary because the electron is supposed to move to the metal electrode. In contrast, the electrons and the holes are transported to the ITO and a metal electrode in an OPV device with an inverted structure. Moreover, PEDOT:PSS, which is inserted into the normal structure to form an ohmic contact between the ITO and the conjugated polymer, is replaced with MoO\(_3\) or V\(_2\)O\(_5\), leading to an increase in the stability of the device. **Figure 1.17** shows the structure of OPV devices with a conventional normal structure and an inverted structure.
Figure 1.17. OPV devices of the normal (top) structure and inverted (bottom) structure.
P3HT:PC_{60}BM-based inverted devices are similar or lower than those of devices with normal structures. However, inverted devices based on new conjugated polymers often exhibit higher performance compared to normal devices. Therefore, an inverted structure is favorable for enhancing the efficiency as well as improving the stability.

1.4 Aim and scope of this research

Based on the theoretical overview and state-of-the-art analysis, issues relating to OPV improvement for next-generation solar cells will be reviewed.

1.4.1 Efficiency enhancement of photovoltaic devices

1.4.1.1 Issue: Limited materials that form self-assembled nanowire

OPV is a device that satisfies most conditions of next-generation solar cells, but it has low PCE compared to other solar cells and commercialization cannot be achieved until performance is enhanced. However, performance enhancement through the synthesis of new materials results in complicating the process and increasing costs. Higher performance may be attained while maintaining the cost competitiveness of OPV by using commercialized materials to improve efficiency via morphology control.

As analyzed in state-of-the-art, cells created from P3HT nanowires prepared using self-assembly do not take on the conventional BHJ structure. Their advantage lies in morphology control as they are capable of adjusting the width and aspect ratio of the polymer domain. Since these nanowires are based on the self-assembly of P3HT, they cannot be applied to new types of conjugated polymers being synthesized today. For morphological control of low bandgap polymers, it is necessary to develop nanowire preparation methods that do not rely on self-assembly.
1.4.1.2 Preparation and characterization of P3HT nanofibers

In chapter 2, I aim to produce nanofibers with a high aspect ratio from P3HT, a widely known conjugated polymer, using a method other than self-assembly. The structural and optical features of the prepared fibers are examined, and compared with materials used in film casting to understand the characteristics of 1D conjugated polymer. When the electron acceptor PC$_{60}$BM is coated on P3HT nanofibers, photoluminescence quenching is needed to prevent recombination of electrons and holes generated from the absorbed light, resulting in diffusion to the P3HT/PC$_{60}$BM interface followed by dissociation.

1.4.1.3 Preparation of highly reproducible photovoltaic devices based on P3HT nanofibers

A major issue in device production is whether the prepared nanofibers are of a reproducible form. In chapter 3, I inspect the reproducibility of nanofibers according to changes in ambient conditions. High reproducibility is sought based on the theoretical framework. A P3HT OPV device is created using the prepared nanowires, and reproducibility is assessed in terms of device performance.

1.4.1.4 Performance of photovoltaic devices based on PCDTBT nanofibers

In chapter 4, nanofiber-forming technology and PCDTBT are used to create OPVs. The diameter of PCDTBT nanofibers should be 20 nm, two times the exciton diffusion length, so as to maintain a similar scale to existing self-assembled nanowires. Air-processing issues, arising from diameter-related performance variation and device production, will be resolved. The enhanced performance of 1D conjugated polymer-
based solar cells will be verified through a comparison with existing solar cells.

1.4.2 Preparation of flexible and long-lifetime photovoltaic devices

1.4.2.1 Issue: incompatibility of conventional encapsulation methods and flexibility

Usually, the encapsulation of an OPV device is performed by the attachment of glass or a gas barrier thin film such as Al₂O₃. However, glass is not compatible with flexible devices, and other inorganic thin films typically have unavoidable pinholes or cracks. Moreover, these encapsulation methods must be performed with ALD or PECVD processes, both of which involve expensive and complicated vacuum systems. Therefore, it is desirable to prepare flexible gas barrier film by solution-processing methods.

1.4.2.2 Preparation and characterization of flexible gas barrier film

Graphene, which is a 2D material among carbon nanomaterials, is known for its gas barrier property that allows even helium atoms to pass through. The high flexibility and gas barrier property of graphene make it a good candidate material for flexible encapsulation films. In chapter 5, I verify performance after developing a graphene-based gas barrier film and applying it to OPV. Lastly, I replace ITO with CNT and develop flexible solar cells containing sp² carbon bonds.
Figure 1.18. Scheme of the sp$^2$-carbon based OPV device and aim of chapters.
1.5 References

43. P. Vanlaeke, A. Swinnen, I. Haeldermans, G. Vanhoyland, T. Aernouts, D.


Part II

Design and Performance of a Nanoweb of a Conjugated Polymer-Nanofiber-Based Active Layer for High-Performance Photovoltaic Devices
Chapter 2. Preparation and Characterization of Electrospun Conjugated Polymer Nanofibers

2.1. Introduction

The efficiency and short circuit current of an OPV cell are directly influenced by the morphology of the active layer.\textsuperscript{1, 2} Charge transport to the electrode is one of the main factors that determine the short circuit current, so the formation of an effective charge transport pathway is an important consideration in the fabrication of OPVs. 1-D materials with a high aspect ratio are known to be useful for building effective charge transport pathways due to their low percolation threshold.\textsuperscript{3, 4} For example, P3HT nanorods are expected to not only form effective charge transport pathways but also to provide a higher charge mobility than P3HT films,\textsuperscript{5} and hence to enable the preparation of OPV cells with high efficiency.\textsuperscript{6}

During the last few decades, the fabrication of 1-D conjugated polymers has been widely studied and as a result various techniques such as nanoimprint lithography,\textsuperscript{7} templating methods,\textsuperscript{5} and self-assembly processes\textsuperscript{8} have been suggested. However, covering a large area with 1-D conjugated polymers is not easy because the first two methods are intrinsically of limited scale and the third method has only been applied to P3HT of the known conjugated polymers because of the variability of the self-assembly behaviors of such materials.\textsuperscript{9} In contrast, the electrospinning technique is comparatively simple and convenient for fabricating 1-D forms of various materials over a large area.\textsuperscript{10} This technique has an additional advantage over spin coating,
which has conventionally been the technique of choice for OPV cell fabrication: the higher throughput obtained with a multi-nozzle and the less waste of materials.\textsuperscript{11, 12} However, to the best of our knowledge electrospun conjugated polymer fibers have never previously been used in the fabrication of OPV cells. The fiber diameter should be as small as possible in order to produce an effective exciton diffusion length; generated electron-hole pairs will soon be annihilated by recombination during diffusion through fibers with large diameters. It is however not easy to prepare homogeneous conjugated polymer nanofibers of diameters below 100 nm through electrospinning. There are several reasons for these difficulties: firstly, conjugated polymer solutions usually have viscosities that are too low for electrospinning, and thus many beads form on the fibers due to Rayleigh instability.\textsuperscript{13} When a high concentration of conjugated polymer is used to provide a high viscosity, the nozzle frequently becomes clogged because the usual solvent for conjugated polymers, i.e., chloroform, evaporates very quickly, and a large amount of conjugated polymer accumulates on the tip of the nozzle. This precipitation of polymer results in the formation of inhomogeneous nanofibers. Some other nonvolatile solvents for conjugated polymers, such as dichlorobenzene and toluene, can be used instead of chloroform but these solutions do not evaporate completely during electrospinning. The use of auxiliary polymers such as poly(ethylene oxide) (PEO)\textsuperscript{14} and poly(methyl methacrylate) (PMMA)\textsuperscript{15} has been suggested with the aim of increasing the viscosity of the electrospinning dope solution. Indeed, the use of an auxiliary polymer does make it possible to electrospin solutions containing low concentrations of conjugated polymers, which prevents clogging. Secondly, since the dielectric constant and conductivity of solvents for conjugated polymers are low, the diameters of the resulting fibers are still of the order of hundreds
of nanometers even when electrospinning without clogging is achieved through the use of an auxiliary polymer.\textsuperscript{14, 15} To obtain thin nanofibers, the solvent used in the spinning of the doped preparation should have a high dielectric constant and high electric conductivity, as is the case for most polar solvents. Thin nanofibers can then be achieved for the following reasons: firstly, the high charge density of the solution hampers the formation of beads due to the electric repulsion force, which means that low concentration solutions can be electrospun to produce thin nanofibers without beads.\textsuperscript{16} Secondly, the high charge density of the solution generates bending instability more easily and thus a whipping cloud forms closer to the nozzle tip, which increases the flight distance remarkably.\textsuperscript{17} A long flight distance means that the solution is stretched more, which leads to fibers with reduced diameters. However, most conjugated polymers do not dissolve in polar solvents, so ultrathin conjugated polymer nanofibers, i.e., with diameters below 100 nm, cannot be obtained. There has been few previous report of conjugated polymer fibers with diameters below 100 nm, which was achieved through electrospinning with a dual nozzle system,\textsuperscript{18, 19} but this approach requires a somewhat complicated set-up and complex spinning conditions.

In this paper, I propose a method for electrospinning thin P3HT nanofibers with diameters below 100 nm that uses a specific co-solvent and an auxiliary polymer to prepare the electrospinning dope solution. As a preliminary test of the use of the resulting nanofibers in an OPV cell, the photoluminescence (PL) performance of a nanoweb consisting of these electrospun ultrathin P3HT nanofibers was examined after bleaching out the auxiliary polymer and subsequently spin-coating PC\textsubscript{60}BM onto the nanofibers. It was found that the PL quenching ratio increases with decreases in the diameter of the P3HT nanofibers: 100% PL quenching arises for a diameter of approximately 80 nm, which confirms that exciton dissociation arises between the...
P3HT nanofibers and PC_{60}BM and that the exciton diffusion length depends on the fiber diameter, even though such diameters are still thick when compared with the theoretical exciton diffusion length. Our results suggest the possible use of these P3HT nanofibers in OPV cells.
2.2. Experimental section

2.2.1. Chemicals and materials
P3HT (Mw 50,000; Rieke metal), PEO (Mw 900,000; Aldrich), poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT; Mw 5,000~8,000; Aldrich), PC_{60}BM (Nano-C), chloroform (Aldrich), acetic acid (Aldrich), N,N’-dimethylformamide (DMF; Daejung, Korea), isopropanol (IPA; Daejung, Korea), acetonitrile (Aldrich), and dichloromethane (Aldrich) were purchased and used without further purification.

2.2.2. Electrospinning
To prepare the electrospinning dope solution, specified amounts of PEO, the auxiliary polymer, and P3HT (or F8BT) were dissolved either separately or together in chloroform with stirring at 50 °C for 6 h. The solutions were electrospun either as prepared or after mixing with various amounts of a polar cosolvent composed of 2 mol of acetic acid and 1 mol of DMF. The compositions of the solutions are specified below in weight percent with respect to the weight of the solvent.

The electrospinning dope solution was loaded into a syringe connected to a metal needle (gauge no. 28, inner diameter 0.18 mm) nozzle and electrospun at a feeding rate of 1.0 mL/h in air at 25~26 °C and 19~21% relative humidity, a bias voltage of 23 kV was applied to the metal needle, and the distance from the nozzle to the grounded collector plate was approximately 21 cm (denoted P3HT@PEO composite nanofibers). For uniform electrospinning, the collector glass plate and the needle nozzle were reciprocated by a 3-axis robot. The as-spun P3HT@PEO composite nanofibers were
subjected several times to various solvents for 30 min to remove PEO and finally virgin P3HT nanofibers were obtained.

2.2.3. Characterization

The morphologies of the P3HT@PEO composite nanofibers and the virgin P3HT nanofibers were examined under a field emission scanning electron microscope (FESEM; JEOL JSM-6330F) operating at an accelerating voltage of 5 kV. The chemical analysis of the P3HT@PEO composite nanofibers were characterized by transmission electron microscope (TEM; Tecnai F20) operating at an accelerating voltage of 200 kV equipped with energy dispersion spectroscopy (EDS). The acquisition time of EDS mapping was 15 minutes and the number of pixels for EDS map was 220 x 220 pixels. The conductivity of each spinning dope solution was measured with an Orion 4-Star pH-Conductivity Meter (Thermo Fisher Scientific Inc.). Thermogravimetric analysis (TGA) was carried out under nitrogen flow with a heating rate of 10 °C /min and isothermal processing at 370 °C for 30 min by using an SDT Q 600 instrument (TA Instruments). The X-ray diffractograms of the nanofibers were recorded in reflection mode, which is standard procedure for X-ray diffraction measurements, by using Ni-filtered Cu Kα radiation (λ = 0.154184 nm) on a D8-Advance diffractometer (Bruker). For comparison, P3HT spin-coated on a silicon wafer was also subjected to X-ray diffractometry. The thickness of the spin-cast film was found to correspond to the amount of electrospun P3HT. The specific surface area was measured with a Micromeritics ASAP 2020 static volumetric gas adsorption instrument at liquid nitrogen temperature (77 K).

2.2.4. PL test
The ultraviolet-visible absorption characteristics of a sample prepared by spin-coating 1 wt% conjugated polymer solution in chloroform onto a glass substrate at 600 rpm were examined by using a Cary 5000 (Varian Inc.).

The photoluminescence properties were examined at the excitation wavelength of 470 nm on an LS-55 (Perkin-Elmer), for which the sample was prepared by spin-coating (a spin rate of 600 rpm) PC$_{60}$BM solution (20 mg PC$_{60}$BM in 1 mL dichloromethane) onto a glass plate covered with virgin P3HT nanofibers.
2.3. Results and discussion

2.3.1. Control of the diameters of the P3HT nanofibers

As mentioned above, it is nearly impossible to prepare homogeneous nanofibers without clogging or bead formation from a spinning dope solution containing only P3HT. Indeed, neither a 2 wt% dope solution (data not shown) nor a 1 wt% dope solution of P3HT could be successfully electrospun (see Figure 2.1(a)). In this situation, an auxiliary polymer can be used to make the electrospinning of P3HT possible. PEO was selected as the auxiliary polymer because of its high viscosity in chloroform and its easy removal by melting at relatively low temperatures, viz. over 70 °C.
Figure 2.1. SEM micrographs of fibers electrospun from spinning dope solutions in chloroform containing (a) 1 wt% P3HT only; PEO only: (b-1) 1 wt%, (b-2) 0.5 wt%, (b-3) 0.25 wt%; P3HT@PEO mixtures: (c-1) 1/1 wt%, (c-2) 0.5/0.5 wt%.
To determine the optimum concentration of PEO, the variation of the electrospinning behaviors of the PEO solutions was examined as a function of the PEO concentration in the spinning dope solution, ranging from 0.15 to 1 wt%. Figures 2.1(b) and 2.1(c) clearly show that the auxiliary polymer content in the spinning dope solution should be above at least 0.5 wt% for both the PEO only and P3HT@PEO mixture solutions in order to obtain composite nanofibers without bead formation. It is however undesirable that the diameter of the obtained nanofibers becomes larger with increases in the PEO content of the spinning dope solution (see Figure 2.2), as discussed in an earlier report.\(^2\) In addition, the fiber formation behavior of the P3HT@PEO mixture solutions is very similar to that of the PEO only solutions, which indicates that PEO plays the dominant role in the electrospinning of the P3HT@PEO mixtures and thus in controlling the diameters of the P3HT nanofibers. This insight makes it possible to electrospin much thinner nanofibers of PEO.
Figure 2.2. Variations in the diameters of the electrospun fibers with the PEO concentration of the spinning dope solutions.
In principle, the electrical conductivity and dielectric constant of the spinning dope solution of PEO in chloroform should be increased in order to obtain thinner nanofibers. Indeed, there have been a few reports of the electrospinning of thin PEO nanofibers with diameters below 100 nm\textsuperscript{23,24} through the use of polar solvents, such as water and acetic acid, that have high electrical conductivity and a high dielectric constant. However, these solvents are inappropriate for electrospinning P3HT because P3HT is not soluble in these solvents.

To address this problem, a polar cosolvent mixture was tested in this study: chloroform was admixed with DMF and acetic acid (2:1 mol/mol) to increase the dielectric constant and viscosity of the dope solution; DMF has a high dielectric constant of 36.69 and a high conductivity of 3.430 $\mu$S/cm, whereas chloroform has a dielectric constant of 4.8 and a conductivity of 0 $\mu$S/cm, and acetic acid increases the viscosity of DMF at a molar mixing ratio of 2:1.\textsuperscript{25} Figure 2.3 clearly shows that increases in the concentration of DMF/acetic acid in the polar cosolvent mixture lead to concurrent increases in the conductivity and decreases in the fiber diameter. Note that too much DMF/acetic acid in the polar cosolvent mixture reduces the homogeneity of the nanofibers because PEO has poor solubility in DMF, which results in the formation of beads on the nanofibers.\textsuperscript{26}
Figure 2.3. The variations in the conductivity of the spinning dope solution and the diameter of the electrospun nanofibers of PEO with the concentration of DMF/acetic acid in the polar cosolvent mixture in the spinning dope solution (concentration of PEO: 0.35 wt%).
Figure 2.4 shows the changes in the morphology of the electrospun nanofibers of PEO with increases in the concentration of DMF/acetic acid in the polar cosolvent mixture in the spinning dope solution. When the spinning dope solution contains 13.3 wt% of DMF/acetic acid, the diameter of the PEO nanofibers is \(~100 \text{ nm}\) without bead formation. Beads form at higher concentrations of DMF/acetic acid (data not shown), and are much larger than the diameters of the fibers. Therefore, the concentration of DMF/acetic acid was fixed at 13.3 wt%.
Figure 2.4. SEM micrographs of the electrospun PEO nanofibers for various concentrations of DMF/acetic acid in the polar cosolvent mixture: (a) 5 wt%, (b) 8.3 wt%, (c) 10 wt%, (d) 13.3 wt%, (e) 16.6 wt%, and (f) 18.3 wt% (concentration of PEO: 0.35 wt%).
P3HT/PEO composite fibers were then electrospun under the abovementioned optimum electrospinning conditions for PEO. In order to find the optimum ratio of PEO to P3HT, the electrospinning behaviors of spinning dope solutions containing various mixing ratios of PEO to P3HT were examined. For a 1:1 mixing ratio, the spinning nozzle became clogged soon after electrospinning had commenced (data not shown). Clogging arises under these conditions because the solubility of P3HT in the polar cosolvent mixture is lower than in pure chloroform. When the mixing ratio was 2.3:1, nanofibers with beads were found to form (see Figure 2.5(a)). However, as can be seen in Figure 2.5(b), at a mixing ratio of 1.4:1 the fibers were successfully electrospun homogeneously over a large area. The P3HT@PEO composite nanofibers were approximately 110 nm in diameter and a few centimeters in length. Table 2.1 lists the morphological characteristics and the average diameters of the P3HT@PEO composite nanofibers. As mentioned above, the beads are much larger than the diameters of the fibers and thus these fibers are inappropriate for our purpose.
Figure 2.5. SEM micrographs of electrospun P3HT@PEO composite nanofibers with various P3HT/PEO ratios (in wt%): (a) 0.15/0.35, (b) 0.25/0.35 (inset: a magnified image with a scale bar of 100 nm), and of electrospun F8BT@PEO composite fibers with various F8BT/PEO ratios (in wt%): (c) 0.25/0.35, (b) 0.15/0.35.
Table 2.1. Morphological characteristics and average diameters of electrospun P3HT@PEO and F8BT@PEO composite nanofibers

<table>
<thead>
<tr>
<th>concentration of PEO (wt%)</th>
<th>concentration of conjugated polymer</th>
<th>morphology of fibers</th>
<th>average fiber diameter (nm)</th>
<th>average bead diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>P3HT 0.05</td>
<td>Beads and fibers</td>
<td>90</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>P3HT 0.15</td>
<td>Beads and fibers</td>
<td>90</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35&lt;sup&gt;a&lt;/sup&gt;</td>
<td>P3HT 0.25</td>
<td>Fibers</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>Washed&lt;sup&gt;b&lt;/sup&gt;</td>
<td>P3HT 0.25</td>
<td>Fibers</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>0.35</td>
<td>F8BT 0.25</td>
<td>Beads and fibers</td>
<td>240</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>F8BT 0.15</td>
<td>Fibers</td>
<td>180</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>P3HT fibers before removal of PEO.

<sup>b</sup>P3HT fibers after removal of PEO.
F8BT is a polyfluorene copolymer that has been used as an electron acceptor in OPV cells.\textsuperscript{27,28} However, F8BT nanofibers have not previously been reported; in this study I attempted to electrospin this polymer by adopting the spinning dope solution with the polar cosolvent mixture used in the electrospinning of P3HT. Homogeneous nanofibers of F8BT (molecular weight: 5,000 ~ 8,000 g/mol) were successfully obtained for a 2.3:1 mixing ratio of PEO:F8BT (see Figure 2.5(d)), whereas elongated bead-like nanofibers were obtained for a 1.4:1 mixing ratio (see Figure 2.5(c)). This result demonstrates that even conjugated polymers with low molecular weights can be electrospun into nanofibers by adjusting the composition of the spinning dope.

To examine the structure of P3HT@PEO composite nanofibers, elemental mapping of the nanofibers using EDS was carried out for sulfur and oxygen that are typical elements of P3HT and PEO. Figure 2.6(a) and 6(b) illustrate the scanning transmission electron microscopy (STEM) image of the nanofibers and the mapping image of the nanofibers, respectively. Due to the low melting temperature (70 °C) of PEO, the STEM and EDS analysis was intentionally performed using very thick (200 nm) fiber. The carbon mapping image shows a typical cylinder-type image, which has high intensity in the middle and low intensity at the edges. In contrast, oxygen mapping image has relatively low intensity in the middle of the fibers because the core of the fibers is occupied mainly by P3HT as depicted in mapping of sulfur image. These elemental mapping images indicate that P3HT and PEO forms each separate domain during electrospinning and build core-shell structure without using complicated dual nozzle system. Having considered that the ratio of the oxygen layer to the sulfur layer in the mapping image is 1:0.74, and the average diameter of P3HT@PEO composite nanofibers is 110 nm, it is expected that P3HT fibers with the
diameter of approximately 80 nm would be obtained after removal of the PEO shell of the composite nanofibers.
Figure 2.6. (a) STEM micrograph of electrospun P3HT@PEO composite nanofiber and (b) EDS mapping with the intensity graph of carbon (green), sulfur (red yellow) and oxygen (purple) on selected area of (a).
Once the core-shell structured P3HT@PEO nanofibers are formed, thin P3HT nanofibers can be obtained after a selective removal of the PEO shell layer. However, there has been little research on the mechanism for the core-shell type structure evolution from P3HT and PEO blends. Earlier works on the core-shell structure formation in other kinds of polymer blends suggested that a phase separation and a solubility difference between the two component polymers can induce such core-shell type structure, but none of those can explain why it should be “P3HT core” instead of “PEO core”. To consider the structure evolution mechanism in detail, I tried to calculate the energy dissipation rate to suggest an energetically stabilized structure with concurrent microphase separation. The calculation of the energy dissipation rate has conventionally been used in predicting a structure evolution during melt spinning of polymer blends. So, basically the same equation as for the melt spinning can be applied to the case of electrospinning, but it needs to take into account the different spinning conditions between the two spinning methods. That is, in melt spinning the directions of the normal stress and the shear stress acting on the flow are opposite to each other but in electrospinning those are approximately in the same direction because of the accumulated charges on the surface of the flow subjected to an electric field. This difference gives rise to an opposite flow velocity profile in each case, viz. concave and convex for the melt spinning and the electrospinning, respectively, to the flow direction. Then from calculation of the energy dissipation rate, using equation (1), for the two representative cases of the flow having (a) low viscosity polymer in the core and (b) high viscosity component in the core,

\[ E \propto \int \eta (\frac{dv}{dr})^2 r dr \]  

(1)
where $\eta$ is viscosity, $\nu$ is velocity, and $r$ is a radial position from the center of a cylindrical flow model,

I can get the solutions for each case as shown in the equations (2a) and (2b), where $E_{\text{hom}}$ is the energy dissipation rate of a low viscosity homogeneous solution, and $H$ is the viscosity ratio of the two polymer solutions ($\eta_{\text{low}}/\eta_{\text{high}}$), and $r^*$ is the radial position of the two polymer phase boundary.

$$\frac{E}{E_{\text{hom}}}=\frac{1-(1-H)(1-r^*_4)}{(1+(1-H)(1-r^*_4)-2(1-H)(1-r^*_3))^2}$$  \hspace{1cm} (2a)$$

$$\frac{E}{E_{\text{hom}}}=\frac{1-(1-H)r^*_4}{(1+(1-H)r^*_4-2(1-H)r^*_3)^2}$$  \hspace{1cm} (2b)$$

As $r^*$ can be expressed as shown in the equations (3a) and (3b) on the constant flow rate condition for both low and high viscous solutions,

$$r^*_2=\frac{1-H+\sqrt{1+H}}{3-H}$$  \hspace{1cm} (3a)$$

$$r^*_3=\frac{1-H-\sqrt{H^2-H}}{1-3H}$$  \hspace{1cm} (3b)$$

the energy dissipation rate can then be expressed by a function of the viscosity ratio, $H$, only, and Figure 2.7 shows the plots of $\frac{E}{E_{\text{hom}}} vs. H$ for the cases (a) and (b). It can be clearly seen from the figure that the energetically favored structure in whole range of $H$ is of the type of low viscosity polymer in the core and high viscosity polymer in the shell. In our case, since P3HT polymer has the lower viscosity than PEO, the energetically favored structure is then formed when P3HT locates in the core while PEO in the shell as observed in figure 2.6.
Figure 2.7. Dependence of energy dissipation rate on the viscosity ratio $H = \frac{\eta_{\text{low}}}{\eta_{\text{high}}}$ between the two polymers.
To utilize these electrospun nanofibers in OPV cells, the auxiliary polymer, PEO, should be removed because its presence degrades the electron transfer efficiency of P3HT nanofibers. Having been considered the solubility of PEO and P3HT, acetonitrile is a good candidate solvent for the selective removal of PEO.\textsuperscript{32} To verify the removal efficiency, thermo-gravimetric analysis (TGA) was used in our experiment. Since PEO is completely degraded at 370 °C under nitrogen flow and P3HT is barely degraded (Figure 2.8), the weight loss during the heat treatment indicates the contents of PEO in the samples. To confirm the method is appropriate for the determination of the removal efficiency of PEO, P3HT@PEO (1.4:1 mixing ratio of PEO:P3HT) composite nanofibers were heat-treated on the condition. Electrospaired P3HT was used as a reference sample for accurate calculation. Indeed, the weight loss of the composite nanofibers was approximately 58.5 wt%, which corresponds well with the theoretically calculated PEO contents of 58.3 wt%. It means that the determination of the PEO removal efficiency with the TGA method is reliable.
Figure 2.8. Thermo-gravimetric thermograms of various samples under isothermal treatment at 370 °C.
According to the TGA analysis, acetonitrile, which was recommended in an earlier report, is not as effective at room temperature. I therefore increased the temperatures above 70 °C, which is the melting temperature of PEO and removal process with other solvents was tested. **Table 2.2** summarizes the PEO removal efficiencies of the solvents. It was found that IPA is the most effective solvent for the removal of PEO from the composite fibers. The morphologies of the nanofibers after PEO removal by using IPA from the P3HT@PEO composite nanofibers (denoted virgin P3HT fibers) are shown in **Figure 2.9**. As can be seen in figures 2.9(a) and (b), the average diameters of the nanofibers are approximately 80 nm, which is the smallest value, to the best of our knowledge, ever reported for single-nozzle-electrospun conjugated polymer fibers. Furthermore, the observed fiber diameter is in very good agreement with the calculated value, 81 nm, from the mapping data in figure 2.6, implying a successful removal of PEO in the shell.
Figure 2.9. SEM micrographs of electrospun virgin P3HT fibers. (a-b) Low and high magnification images (inset: scale bar 100 nm), and (c-d) larger diameter P3HT electrospun fibers.

Table 2.2. The PEO residues in the P3HT@PEO composite nanofibers after dipping into various solvents maintained at temperatures above 70 °C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Acetonitrile</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Isopropanol</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of PEO residue (%)</td>
<td>4.9±0.4</td>
<td>2.8±0.3</td>
<td>0.9±0.1</td>
<td>0( ^a )</td>
<td>2.4±0.4</td>
</tr>
</tbody>
</table>

\( ^a \) Negligibly small.
To examine the effects of diameter variation on the opto-electric properties of the nanofibers, fibers with larger diameters were also prepared by adjusting the concentrations of polymer and the polar cosolvent mixture in the spinning dope solution. Figures 2.9(c) and (d) show virgin P3HT nanofibers with average diameters of approximately 290 and 460 nm respectively. Note that although the nanofibers’ surfaces appear rather irregular, PEO removal does not lead to a significant deterioration of the fiber morphology.

### 2.3.2 Optical properties of the nanofibers

**Figure 2.10** (a) shows the absorption spectra of electrospun P3HT fibers with a diameter of 80 nm and a spin-coated P3HT film. The spectrum of the electrospun nanofibers is red-shifted by 15~20 nm with respect to that of the film, and contains stronger absorption at 600 nm. Indeed, for the P3HT nanofibers the intensity ratio of the peak near 550 nm to that near 600 nm is 1.23, which is much higher than the ratio of 0.63 for the spin-coated film. I believe that the electric field applied during electrospinning induces these two optical features of the P3HT fibers: the P3HT polymer chains are more or less extended along the applied electric field, which means that the conjugation length is extended and leads to a red-shifted absorption spectrum, and the crystallinity of the fiber is also increased. Indeed, **Figure 2.11** confirms that the electrospinning process facilitates the crystallization of P3HT. These results have the practical consequence that P3HT nanofibers can harvest more photons than P3HT films. In fact, much research effort has been applied to increasing the photon harvest capability of conjugated polymers through the use of newly synthesized low-bandgap polymers. However, the synthesis of new polymers with outstanding electrical and photonic properties is time-consuming and laborious. Thermal annealing
is the one way of enhancement of photon harvest without synthesis of new polymers because it induces red-shifted absorption via crystallization of P3HT. Likewise, electrospinning provides a route to preparing materials with high crystallinity and photon harvesting capabilities. Furthermore, it is generally accepted that increasing the crystallinity of P3HT contributes to better electron transport. Thus, the electrospinning of P3HT nanofibers can potentially make possible not only the efficient harvesting of photons but also excellent charge transport without thermal treatment.
Figure 2.10. UV-Visible absorption spectra of (a) virgin P3HT fibers (red dashed line) and a P3HT film (black solid line) and (b) virgin F8BT fibers (red dashed line) and a F8BT film (black solid line) (inset: spectra magnified in the range 440–500 nm). (Normalized with respect to maximum intensity of each graph, scattering effect was corrected using PEO fibers).
Figure 2.11. XRD patterns of the virgin P3HT nanofibers (black) and the spin-cast P3HT film (red).
In the case of F8BT, the absorption spectrum of the electrospun nanofibers is also red-shifted with respect to that of the film (Figure 2.10(b)), but the extent of the red shift is only approximately 4 nm. This difference between the red shifts is probably due to the low molecular weight of F8BT, which limits the increase in the conjugation length that is achieved by the application of an electrical potential during electrospinning.

### 2.3.3. Photoluminescence quenching

To test the applicability of the virgin P3HT nanofibers to OPV cells, the photoinduced charge transfer (PICT) efficiency was examined by measuring their photoluminescence quenching behavior, which is an indication of the dissociation of an exciton into an electron and a hole. PL quenching occurs at the interface between P3HT and PC_{60}BM and the diffusion length of the exciton is very limited, so the PL quenching behavior is expected to vary with the diameter of the electrospun P3HT nanofibers. Figure 2.12 shows that the PL quenching of the virgin P3HT nanofibers increases with decreasing fiber diameter, from ~25% for nanofibers with a diameter of 460 nm through to ~40% for a diameter of 280 nm and ~100% for a diameter of 80 nm.
Figure 2.12. PL quenching properties of virgin P3HT nanofibers with various diameters: P3HT nanofibers only (80 nm, black squares); composite films of PC$_{60}$BM with P3HT nanofibers (460 nm, red circles; 290 nm, green triangles; 80 nm, blue triangles).
The exciton diffusion length in P3HT is approximately 10 nm, so it is interesting to note that approximately 100% PL quenching is achieved with the 80 nm virgin P3HT nanofibers. It is speculated that formation of interphase layer and feature of electrospun nanofibers are responsible for high PL quenching. Indeed, a recent work suggested that much increased (up to approximately 90%) PL quenching behavior of a spin-cast P3HT/PC₆₀BM bilayer film is due to the interphase formation between P3HT and PC₆₀BM, which is facilitated by the solvent, viz. dichloromethane. In addition Wang et al. also reported that PC₆₀BM diffuses into the P3HT layer swollen by dichloromethane to form interphase layers of which thickness is about 40 nm. Having been considered that I also used dichloromethane as the solvent and the radius of the virgin P3HT nanofibers is approximately 40 nm the whole part of our nanofibers is expected to participate in the interphase formation. In addition, much increased surface area of the nanofibers (15 m²/g SSA, calculated using the BET equation on the N₂ adsorption isotherm) compared to that of the film (3 m²/g SSA) allows for solvent molecules to effectively create interphase layer over a large area. Furthermore, it has been reported that the longer exciton lifetime and improved energy transfer are achieved in the electrospun conjugated polymer. It is thus expected that the effective exciton diffusion length in the electrospun P3HT fibers be longer than in P3HT films.
2.4. Conclusions

In this study, a nanoweb consisting of P3HT nanofibers was successfully prepared via single-nozzle-electrospinning of a spinning dope solution containing PEO as an auxiliary polymer in a polar cosolvent mixture composed of chloroform, DMF, and acetic acid. After the PEO was completely removed, the diameter of the resulting virgin P3HT nanofibers was found to be approximately 80 nm. The photoluminescence of the nanoweb of the virgin P3HT nanofibers was found to be quenched by approximately 100% when PC_{60}BM was coated onto the nanofibers, which indicates that photoinduced electrons are successfully transferred. This feature of the nanoweb consisting of P3HT nanofibers with a diameter of 80 nm is acceptable for OPV cells. As it is expected for the nanowebs to exhibit several advantageous features such as a wide range of light absorption and effective dissociation of excitons, further research will be devoted to the preparation of OPV cells composed of conjugated polymer nanowebs.
2.5. References

Chapter 3. Highly Reproducible Electrospun Conjugated Polymer Nanofibers Based Photovoltaic Devices

3.1. Introduction

Electrospinning is a facile and effective method for processing solutions into continuous fibers having diameters that can range from a few nanometers to a few micrometers. The high aspect ratios and surface areas of electrospun fibers render them useful for a variety of applications, including filters, batteries, and catalysts. The electrospinning technique was recently applied toward the preparation of electronic devices, such as organic thin film transistors, sensors, and OPV devices based on conjugated polymer nanofibers. 1-D materials with high aspect ratios have several advantages over conventional film-based materials in electronic devices: 1) 1-D materials form a continuous charge transport pathway, 2) provide enhanced electrical properties, and 3) offer a high surface area. Conjugated polymer nanofibers prepared by electrospinning technique, therefore, can contribute to the preparation of high-performance devices. OPV devices prepared using electrospun fibers display particularly high performances, as reported previously.

Electron-hole pairs, called excitons, have high binding energy in organic materials. To dissociate excitons in a conjugated polymer, the active layer of OPV devices consist of electron donor and acceptor materials. A large surface area at the heterojunction of the electron donor and acceptor materials is required to facilitate the effective dissociation of excitons. Electrospun conjugated polymer nanofibers are useful for improving the performances of OPV devices because electrospun nanofibers offer a high surface area.
high specific surface area,\textsuperscript{9, 14} which increases the interface between the conjugated polymer and the PC\textsubscript{60}BM. The continuous morphology of the electrospun fibers facilitates dissociated charge transport. Exciton dissociation and charge transport in an active layer can directly influence the photocurrent in the OPV devices. Electrospun OPV devices exhibit an enhanced short circuit current (J\textsubscript{SC}) and power conversion efficiency.

The reproducibility of a device is an important issue in the fabrication of OPV devices. Although electrospun OPV devices may generally be produced with good reproducibility, their performances can be poor when prepared during certain seasons. Figure 3.1 shows the current density–applied voltage (J-V) curve, measured in our laboratory, for an electrospun poly P3HT nanofiber-based ITO/PEDOT:PSS/P3HT/P3HT nanofiber/PC\textsubscript{60}BM/TiO\textsubscript{x}/Al OPV device. The J\textsubscript{SC} and PCE of the cell 1 exceeded the values obtained from a bilayer-structured OPV device (Figure 3.2), similar with the results obtained previously from a PCDTBT nanofibers-based OPV device.\textsuperscript{10} The J\textsubscript{SC} of cell 2, however, was much lower than the value obtained from cell 1, even though these two cells were prepared from identical spinning dope solutions. The preparation conditions of cell 1 and those of cell 2 differed due to the seasonal differences in the environmental conditions during device fabrication. Cell 1 and cell 2 were prepared during the dry season and the humid season, respectively. The bilayer structured OPV devices were fabricated at the same times as cells 1 and 2; however, they displayed similar efficiencies (Figure 3.2). This result suggested that the electrospinning process introduced the performance variations. The fluctuations in the performances of devices prepared using electrospinning techniques reduced the reliability of the electrospinning process as a practical fabrication procedure. Small changes in the ambient conditions have been shown to induce large
differences in the properties of products prepared using electrospinning techniques. The main reasons and mechanisms underlying the fluctuations must be investigated in detail, and approaches for increasing the reproducibility and reliability must be developed.
Figure 3.1. J-V curves obtained from the electrospun OPV devices prepared from the P3HT nanofibers fabricated during the dry season or the humid season.

Figure 3.2. J-V curves obtained from the electrospun OPV device and bilayer cells fabricated during the dry season or the humid season.
The diameters of the nanofibers can influence the performance of an electrospun OPV device;\textsuperscript{9,10} therefore, the nanofibers of the two cells may potentially have presented different morphologies and diameters. Differences in the ambient conditions associated with the dry or humid seasons were expected to change the morphology and diameter of the electrospun fibers, thereby influencing the performances of the OPV devices. This work investigated the effects of the ambient conditions on the morphologies of the electrospun fibers. The photovoltaic performances were examined and experimental conditions that would help avoid a reduction in efficiency were designed and tested.
3.2. Experimental Section

3.2.1. Chemicals and materials

P3HT (Mw 50,000; Rieke metal), PEO (Mw 900,000; Aldrich), PEDOT:PSS (Clevios P VP Al 4083, H.C. Stark), PC_{60}BM (Nano-C), chloroform (Aldrich), acetic acid (Aldrich), DMF (Daejung, Korea), acetonitrile (Aldrich), titanium isopropanoxide (Aldrich), methanol (Aldrich), and dichloromethane (Aldrich) were purchased and were used without further purification.

3.2.2. Electrospinning

The electrospinning process is described in a previous paper. A solution containing 0.35 wt% PEO and 0.15 wt% P3HT, dissolved in chloroform, was stirred at 50°C for 6 h. A polar cosolvent consisting of acetic acid and DMF (in a molar ratio of 2:1) was added to the solution (in a 1:8 weight ratio). The electrospinning dope solution was loaded into a syringe connected to a metal needle (gauge no. 28, inner diameter 0.18 mm) nozzle and was electrospun at a feeding rate of 1.0 mL/h in air. A bias voltage of 25 kV was applied to the metal needle, and the distance from the nozzle to the grounded collector plate was fixed at 21 cm (denoted P3HT@PEO composite nanofibers). Uniform electrospinning was achieved by reciprocating the collector glass plate and the needle nozzle using a 3-axis robot. The as-spun P3HT@PEO composite nanofibers were exposed to acetonitrile several times for 30 min periods to remove any PEO. Finally, virgin P3HT nanofibers were obtained. Warm air was applied to the electrospun fibers using a small heater (MFH-3615, JL Home) during the electrospinning process.
3.2.3. Fabrication of the OPV devices

ITO/glass substrates were cleaned by sonication in detergent, acetone, and IPA. The ITO substrates were then treated with UV/ozone for 15 min, and PEDOT:PSS was spin-cast at 5000 rpm for 40 s. The PEDOT:PSS films were dried at 150°C for 15 min. A 10 nm P3HT layer was then spin-coated onto the PEDOT:PSS layer. P3HT nanofibers were prepared according to the method described above, and the PC_{60}BM layer was spin-cast onto the active layer at 5000 rpm for 20 s from a dichloromethane solution with a concentration of 16 mg/mL. A TiO_{x} precursor solution was prepared as described previously. The solution was spin-cast onto the top of the active layer at 5000 rpm for 40 s. A 100 nm thick aluminum cathode was then deposited using a thermal evaporator. The devices were heat-treated at 150°C for 30 min under vacuum. The PCE values of the devices were determined using a K3000 instrument (McScience).

3.2.4. Characterization

The morphologies of the P3HT@PEO composite nanofibers and the virgin P3HT nanofibers were examined using a field emission scanning electron microscope (FESEM; JEOL JSM-6700F) operated at an accelerating voltage of 5 kV. The photoluminescence properties were examined at an excitation wavelength of 470 nm using an LS-55 (Perkin-Elmer). The evaporation rate was evaluated in an electrospinning chamber based on the measured weight change.
3.3 Results and discussion

The nature of the low efficiency of cell 2 was explored by first investigating the morphology of the electrospun P3HT@PEO composite fibers. Figure 3.3 shows an image of the electrospun fibers that had been incorporated into cells 1 and 2. The electrospun P3HT@PEO composite fibers prepared for cell 1 and cell 2 clearly differed in their morphologies. The P3HT@PEO composite fibers used to prepare cell 2 included many beads on the fiber surfaces, and the beads remained after the PEO had been removed from the composite fibers. The beaded morphology can be useful in some applications, but it was undesirable for the OPV cells prepared here. The average bead diameter was 200 nm, much higher than the exciton diffusion length. The excitons generated in the beads tended to recombine because they could not reach the interface between the P3HT and PC60BM layers. The PL of the active layer in cell 2 was, therefore, not fully quenched (Figure 3.4). The low performance of cell 2 resulted from the poor morphologies of the electrospun fibers and the active layer.
Figure 3.3. SEM micrographs of the P3HT@PEO composite fibers (a and b) and of the virgin P3HT fibers (c and d). Fibers were electrospun in the dry season (a and c) or in the humid season (b and d).
Figure 3.4. PL properties of the virgin P3HT nanofibers and the composite films composed of PC$_{60}$BM and virgin P3HT nanofibers.
The assumption that the ambient condition influenced the morphology and performance of the nanofibers-based device was explored by measuring the temperature and relative humidity (RH) of the ambient conditions during fabrication of cell 1 (dry season) and 2 (humid season). Although the temperatures of the two seasons remained the same, 25°C, the RH values of the dry and humid seasons were 21% and 48%, respectively. The large difference in the RH of the seasons could have contributed to the morphological differences in the electrospun fibers. The effects of humidity on the electrospinning were explored in detail by electrospinning the nanofibers under different ambient conditions (20%, 30%, 40%, and 50% RH). Figure 3.5 and Figure 3.6 shows SEM images of the nanofibers obtained from identical spinning dope solutions. The average diameter and standard deviation of the nanofibers are summarized in Table 3.1 and Figure 3.7. The electrospun fibers fabricated at higher RH tended to form beads on the fiber surfaces, and the fiber diameter tended to be lower. The average diameters of some of the beads on the fibers prepared at 50% RH exceeded 500 nm and were thicker than the active layer of the OPV device. Aggregated regions in a BHJ structure have been reported to reduce the cell efficiency. Reducing the humidity was found to help reduce the number and size of the beads. The beads were not observed in electrospun fibers prepared at 20% RH.
Figure 3.5. SEM images of electrospun P3HT@PEO composite fibers prepared at (a) 20%, (b) 30%, (c) 40%, and (d) 50%.
Figure 3.6. SEM images of electrospun P3HT fibers prepared at (a) 20%, (b) 30%, (c) 40%, and (d) 50%.
Table 3.1. Variations in the diameters of the electrospun fibers and beads as a function of the RH.

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>Diameter of fibers (nm)</th>
<th>Diameter of beads (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>118.8 ± 19.5</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>83.3 ± 18.4</td>
<td>186.8 ± 47.7</td>
</tr>
<tr>
<td>40</td>
<td>60.3 ± 26.8</td>
<td>241.4 ± 49.1</td>
</tr>
<tr>
<td>50</td>
<td>44.3 ± 13.3</td>
<td>301.5 ± 48.1</td>
</tr>
</tbody>
</table>
Figure 3.7. Variations in the diameters of the electrospun fibers and beads as a function of the RH.
The effects of the fiber morphology on the performances of OPV devices prepared from the electrospun P3HT nanofibers fabricated under the ambient conditions listed in Table 3.2 were explored. The power conversion efficiency was found to be inversely related to the RH. The open circuit voltages of the OPV devices were similar, regardless of the RH; however, the $J_{SC}$ and fill factor (FF) of the OPV devices depended significantly on the RH. Poor exciton dissociation and recombination from the large beads may yield a poor $J_{SC}$ and FF. These experimental results indicated that the performances of the electrospun OPV devices depended on the ambient conditions because the morphologies of the electrospun fibers were quite sensitive to the RH. Because the maintenance of a low RH tends to be difficult during the humid season, the humidity-dependent morphological variations reduced the reliability of the electrospinning method for the preparation of nanofibers for use in electronic applications beyond OPV devices. Additional efforts are required before homogeneous electrospun fibers with small diameters may be successfully prepared during the humid season, and the role of humidity on the electrospinning product needs further investigation.
Table 3.2. Performances of the OPV devices prepared using PCDTBT nanofibers with various diameters.

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.604</td>
<td>7.00</td>
<td>50.2</td>
<td>2.12</td>
</tr>
<tr>
<td>30</td>
<td>0.546</td>
<td>5.12</td>
<td>45.0</td>
<td>1.26</td>
</tr>
<tr>
<td>40</td>
<td>0.497</td>
<td>4.01</td>
<td>37.7</td>
<td>0.75</td>
</tr>
<tr>
<td>50</td>
<td>0.439</td>
<td>2.19</td>
<td>30.9</td>
<td>0.30</td>
</tr>
</tbody>
</table>
RH has been recognized as one of the experimental parameters that can most strongly influence the performances of electrospun fibers;\textsuperscript{15-18} however experimental studies have pointed to a range of humidity effects. Previous studies reported that electrospun fibers prepared under high RH conditions displayed small-diameter fibers\textsuperscript{15} with porous surfaces\textsuperscript{18} and a fused morphology.\textsuperscript{17} Other studies reported the development of a phase-separated structure. On the other hand, the high humidity conditions applied in the present study resulted in the preparation of beaded electrospun nanofibers with small diameters. Despite the generation of different fiber morphologies, the evaporation behavior of the solvent at high RH must contribute to the morphology effects. Because RH is defined as the ratio of the amount of water vapor in the air to the saturating amount of water in the air at a specific temperature, a high partial pressure of water vapor in the air at a high humidity can prevent the evaporation of water during electrospinning. Slow evaporation is thought to allow a water-based spinning dope solution sufficient time to stretch, thereby producing fibers with small diameters. On the other hand, a longer stretching time could provide time to form beads due to Rayleigh instabilities in the solution. A small fiber diameter and the formation of beads appear to be inseparable features of the electrospinning technique. The experimental results in this study supported these general principles.

The discussion presented in the previous section relied on the fact that the water evaporation rate depends on the humidity; however, the solvent used in the electrospinning system discussed here was chloroform. It was not clear whether the evaporation rates of solvents other than water were affected by the RH. Fundamentally, the RH should only influence the evaporation of water because the process of returning water molecules in the ambient air to the water surface will decrease the evaporation rate of water, but not of other solvents. Nevertheless, alcohol-based spinning dope
solutions have been known to spin fibers with small diameters at a high RH, suggesting that the alcohol evaporation rate is also influenced by the RH. Changes in the alcohol evaporation rate may be induced by the adsorption of water molecules to the surface of the alcohol at high humidities.\textsuperscript{19} The adsorption of water molecules may also occur on surface of the chloroform solution, thereby preventing the evaporation of the chloroform. To the best of our knowledge, the RH-dependent chloroform evaporation rate has not previously been investigated. I therefore measured the evaporation rates of water, ethanol, and chloroform under different RH conditions to investigate the effects of RH on the three solvents. \textbf{Table 3.3} and \textbf{Figure 3.8} present the evaporation rates of the three solvents at 20, 30, 40, and 50\% RH. Because the vapor pressure of the chloroform is smaller than that of ethanol and water, chloroform showed the highest evaporation rate under all conditions. The high chloroform evaporation rate formed beadless electrospun fibers from a low spinning dope solution concentration (~0.35 wt\%). A humidity-dependent evaporation rate was observed for both chloroform and ethanol, as well as for water. All solvents examined in this experiment exhibited low evaporation rates under high RH conditions. These results indicated that the water molecules in the ambient atmosphere prevented the evaporation of water as well as other solvents. These results suggested that high humidity conditions provide spinning dope solutions ample time for stretching and/or bead formation before the fiber morphology sets (\textbf{Figure 3.9}). This effect is observed for both aqueous and non-aqueous dope solutions.
Table 3.3. Variations in the solvent evaporation rate under different RH conditions.

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>Chloroform (g/s·m²)</th>
<th>Ethanol (g/s·m²)</th>
<th>Water (g/s·m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.835</td>
<td>0.194</td>
<td>0.0361</td>
</tr>
<tr>
<td>30</td>
<td>0.678</td>
<td>0.149</td>
<td>0.0300</td>
</tr>
<tr>
<td>40</td>
<td>0.651</td>
<td>0.142</td>
<td>0.0263</td>
</tr>
<tr>
<td>50</td>
<td>0.650</td>
<td>0.139</td>
<td>0.0243</td>
</tr>
</tbody>
</table>
Figure 3.8. Variations in the solvent evaporation rate under different RH conditions.
Figure 3.9. Schematic of electrospinning process under low (left) and high (right) RH.
Some studies have reported that the diameters of electrospun fibers fabricated under high humidity conditions are consistently small with uniform morphologies.\textsuperscript{15} In this experiment, however, both the diameter and morphology of the fibers were observed to differ under low and high RH conditions. A 0.35 wt\% dope solution was required for the creation of a bead–fiber morphology; therefore, slight changes in the conditions may induce significant morphological changes. Indeed, fibers electrospun from a 0.5 wt\% PEO solution formed few beads on the fibers, even at a high RH (Figure 3.10), despite the longer drying time, because the high viscosity of the 0.5 wt\% PEO solution (21.09 cP) compared with the 0.35 wt\% solution (9.53 cP) resisted the formation of beads. Highly concentrated spinning dope solutions are generally not appropriate for the preparation of nanofibers.
Figure 3.10. SEM image of electrospin PEO fibers prepared from 0.5 wt% spinning dope solution at 50% RH.
The high-RH conditions during the humid season reduce the solvent evaporation rate and enable the generation of beads on the electrospun fibers. A high evaporation rate is necessary for the production of bead-free electrospun fibers; however, expensive systems are required for the maintenance of a very low RH (< 20%) during a humid season, thereby undercutting one of the primary merits of the electrospinning technique. Blowing warm air across the fibers during electrospinning provides an alternative method for increasing the evaporation rate of the solvent. Heated air streams have been used in conventional dry spinning systems to induce the rapid evaporation of solvents. I simply directed warm air (50°C) over the electrospinning system using a small heater and increased the evaporation rate of the chloroform to 2.15 g/s·m². This rate exceeded the evaporation rate obtained at 20% RH, suggesting that the beadless morphology may be achieved during the humid season using a facile and inexpensive system. **Figure 3.11** shows the morphologies of the electrospun fibers fabricated using the heater during the humid season. The beads were completely absent from the fiber surfaces, and the average fiber diameter was similar to the diameters of fibers obtained at 20% RH. This result clearly indicated that the simple heating system can address the poor reproducibility of the electrospinning technique during the humid season. A schematic of rapid evaporation and formation of beadless fibers under a heater system is illustrated in **Figure 3.12**.
Figure 3.11. SEM micrographs of the P3HT@PEO composite fibers prepared from spinning dope solutions having a (a) 0.35 wt%, (b) 0.3 wt%, or (c) 0.25 wt% PEO concentrations, spun under a heater system.

Figure 3.12. Schematic of electrospinning process under a heater system.
I assumed that the slow solvent evaporation rate under high RH conditions provided ample time for the formation of beads due to the Rayleigh fluid instabilities. If this assumption were correct, the high evaporation rate achieved using the heater system was expected to prevent the formation of beads on the electrospun fibers prepared from spinning dope solutions with concentrations lower than 0.35 wt%, which marks the concentration threshold for transitioning from beadless (concentrations exceeding 0.35 wt%) to beaded (concentrations less than 0.35 wt%) fibers at 20% RH. Indeed, beads formed on the fibers electrospun from 0.3 wt% and 0.25 wt% solutions (Figure 3.13) but were absent or reduced from the fibers prepared from the same solutions under the application of the heater system (see Figures 3.10(b), (c)). The concentration threshold for bead formation depended sensitively on the evaporation behavior and could be controlled through systematic tuning. This approach has practical significance for fibers prepared from spinning dope solutions having low concentrations as a result of other processing constraints, such as limited polymer solubility.

OPV devices prepared using the electrospun fibers were tested to measure the influence of the morphological changes on the OPV performance. The nanofibrous OPV devices prepared using the heater system and the OPV devices prepared during the dry season exhibited similar performances (Figure 3.14). Figure 3.13 clearly indicates that the heater system successfully recovered the device performance. Application of the heater system during the humid season increased the JSC and power conversion efficiency from 2.19 mA/cm² and 0.30% to 7.01 mA/cm² and 2.07 %, respectively (Table 3.4). The method proposed in this study successfully recovered the morphology of the electrospun fibers and their photovoltaic performances. It should be noted that the effects of the active layer P3HT morphology on the photovoltaic performance might also be investigated using the application of heat as a means for
controlling the morphology. This system may be applied to any application that relies on electrospun fibers, to improve the reproducibility or prepare bead-free fibers during a humid season.
Figure 3.13. SEM micrographs of the P3HT@PEO composite fibers prepared from spinning dope solutions having a (a) 0.3 wt%, or (c) 0.25 wt% PEO concentrations at 20% RH.

Figure 3.14. J-V curves obtained from the electrospun OPV devices prepared from the P3HT nanofibers prepared during the dry season or with heating during the humid season.
Table 3.4. Performance properties of the OPV devices prepared using PCDTBT nanofibers with various diameters.

<table>
<thead>
<tr>
<th></th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell (Dry)</td>
<td>0.603</td>
<td>7.00</td>
<td>50.2</td>
<td>2.12</td>
</tr>
<tr>
<td>Cell (Heater system)</td>
<td>0.611</td>
<td>7.01</td>
<td>48.5</td>
<td>2.07</td>
</tr>
</tbody>
</table>
3.4. Conclusions

I investigated the effects of the humidity on the morphologies of electrospun fibers and the performance of OPV devices. A high humidity was found to reduce the solvent evaporation rate, whether the solvent was chloroform or water. Low evaporation rates induced Rayleigh instabilities that generated beads on the surfaces of the electrospun fibers. OPV devices prepared using beaded fibers exhibited a poor device efficiency due to low $J_{SC}$ and FF values. The application of warm air onto the electrospinning system during operation enhanced the solvent evaporation rate and prevented the formation of beads on the electrospun fibers. OPV devices prepared using the beadless P3HT nanofibers displayed high $J_{SC}$, FF, and power conversion efficiencies.

The results of this study revealed that the evaporation rate depended on the ambient conditions and significantly influenced the morphology of the electrospun fibers, thereby reducing the reproducibility of the method. The heating method proposed here is simple, inexpensive, and effective for recovering the beadless morphologies of electrospun fibers, even during the humid season, by increasing the evaporation rate.

Most importantly, this system can be used in both OPV devices and in OTFTs, sensors, and other applications employing electrospun nanofibers.
3.5. References

2012, 134, 15869-15879.


Chapter 4. Preparation and Performance of PCDTBT Nanofibrous Photovoltaic Devices

4.1. Introduction

OPV devices have gained much attention due to low-cost processing and short energy payback time. The performance of an OPV cell is strongly affected by the morphology of the active layer. The development of BHJ structures has greatly increased the efficiencies of OPV cells by enabling the preparation of large donor/acceptor interface areas and bicontinuous charge pathways that facilitate exciton dissociation and charge transport. A variety of approaches have been used to control the morphology of a BHJ structure, including thermal annealing, solvent annealing, and solvent additives. Nevertheless, BHJ OPV devices intrinsically suffer from the presence of unfavorable morphological features, including dead ends or isolated domains, because the procedure used to fabricate BHJ structures offers little control over the morphology of the active layer. Methods for preparing perfectly interconnected morphologies that yield enhanced exciton dissociation and charge extraction have remained elusive. The above-mentioned problems may be addressed using a 1-D conjugated polymer, such as a polymer nanowire or nanofiber, in the active layer. The 1-D conjugated polymer provides a rational approach for controlling the active layer morphology by tuning the diameters and lengths of the rod. Indeed, P3HT nanowires have been extensively studied as the donor component in the active layer of OPV cells. The dimensions of the P3HT nanowires include a width of 20 nm and a length of 10 μm. The reported diameters of the P3HT nanowires agreed well with the exciton diffusion lengths in organic materials, and the high aspect ratio of the P3HT nanowires...
allowed them to easily form a continuous pathway. P3HT can form nanowires in marginal solvents or poor solvents that induce the self-assembled of P3HT into nanowires. Because self-assembly is only observed in thiophene polymer derivatives, the method cannot be applied to new conjugated polymers, e.g. PCDTBT. Alternative fabrication procedures that yield new conjugated polymer nanowires are strongly required for the preparation of photovoltaic devices. Such nanowires are expected to enhance exciton dissociation and charge transport.

Electrospinning is one of the most powerful techniques for spinning polymers or ceramic precursors into continuous fibers with an ultrahigh aspect ratio (> 100,000). The high aspect ratio makes electrospun fibers attractive for many applications. Here, I report, for the first time, the preparation of highly efficient OPV devices based on PCDTBT nanofibers/PC70BM ([6,6]-phenyl-C71-butyric acid methyl ester) prepared by electrospinning in ambient air. The performances of the OPV devices were significantly influenced by the diameters of the nanofibers. The smallest diameter of the PCDTBT nanofibers fabricated in this experiment was 20 nm, which is comparable to the diameters of the self-assembled P3HT nanowires. An OPV device composed of PCDTBT nanofibers with diameters smaller than 20 nm exhibited a higher device performance that was achieved using pseudo-bilayer and BHJ devices fabricated in our laboratory. The OPV cell based on the PCDTBT nanofibers displayed a short-circuit current density ($J_{SC}$) of as high as 11.54 mA/cm$^2$, demonstrating outstanding exciton dissociation and charge transport, even under ambient fabrication conditions.
4.2. Experimental Section

4.2.1. Chemicals and materials
PCDTBT (Mw 30,000; 1-Material), PEO (Mw 900,000; Aldrich), PC70BM (1-Material), PEDOT:PSS (Clevios P VP Al 4083, H.C. Stark), chloroform (Aldrich), acetic acid (Aldrich), DMF (Daejung, Korea), acetonitrile (Aldrich), and dichloromethane (Aldrich) were purchased and used without further purification.

4.2.2. Fabrication and characterization of the nanofibers
The spinning dope solution was prepared by dissolving PEO and PCDTBT (0.4 wt%; 0.1 wt%) in chloroform/polar solvent (8:1, w/w). The spinning dope solution was electrospun at a feeding rate of 0.5 mL/h in air at 25°C, under an atmosphere containing 20% relative humidity. The metal needle (gauge no. 28, inner diameter 0.18 mm) nozzle was connected to a bias voltage of 25 kV, and the distance from the nozzle to the grounded collector plate was 21 cm. The collector glass plate and the needle nozzle were reciprocated using a three-axis robot. The PCDTBT@PEO nanofibers were washed in acetonitrile repeatedly to remove PEO, yielding virgin PCDTBT nanofibers. The morphologies of the nanofibers were examined using a field emission scanning electron microscope (FESEM; JEOL JSM-6700F) operated at an accelerating voltage of 5 kV, and using a transmission electron microscope (TEM; Tecnai F20) operated at an accelerating voltage of 200 kV. The viscosities of the spinning dope solutions were measured using an Orion 4-Star pH-Conductivity Meter (Thermo Fisher Scientific Inc.). TGA was carried out under a nitrogen flow with a heating rate of 10°C/min, and isothermal processing was conducted at 370°C over 30 min using an SDT Q 600 instrument (TA Instruments). The specific surface area was measured with
a Micromeritics ASAP 2020 static volumetric gas adsorption instrument at liquid nitrogen temperature (77 K). The ultraviolet–visible absorption characteristics were examined using a Cary 5000 (Varian Inc.). The photoluminescence properties were examined at an excitation wavelength of 550 nm on an LS-55 (Perkin-Elmer).

4.2.3. Fabrication and characterization of the OPV devices

ITO/glass substrates were cleaned by sonication in detergent, acetone, and IPA. The ITO substrates were then treated with UV/ozone for 15 min, and PEDOT:PSS was spin-cast at 5000 rpm for 40 s. The PEDOT:PSS films were dried at 150°C for 15 min, and then a 10 nm PCDTBT layer was spin-coated onto the PEDOT:PSS layer. PCDTBT nanofibers were prepared according to the method described above, and the PC70BM layer was spin-cast onto the active layer at 5000 rpm for 20 s from a dichloromethane PC70BM solution with a concentration of 16 mg/mL. The total exposure time in ambient air for the nanofibrous devices was 1.5 hours. A TiO$_X$ precursor solution was prepared according to previous reports.$^{27}$ The solution was spin-cast onto the top of the active layer at 5000 rpm for 40 s. The sample was heat-treated at 80°C for 10 min under vacuum. Following this, a 100 nm thick aluminum cathode was deposited using a thermal evaporator. The active layers of the BHJ OPV devices were prepared from a chlorobenzene solution of PCDTBT:PC$_{70}$BM (1:4 w/w) with a total concentration of 20 mg/mL. The active layers of the pseudo-bilayer OPV devices were prepared by sequentially spin-coating PCDTBT (4 mg/mL in chlorobenzene) and PC$_{70}$BM (16 mg/mL in dichloromethane). The devices for measuring the hole mobility were fabricated using the same process except that the TiO$_X$/Al layer was substituted with a Au layer. All processes were performed in ambient air. The PCE values of the
devices were determined using a K3000 (McScience). The cross-sectional TEM samples were prepared by focused ion beam (FEI Helios 650) slicing and observed using TEM (JEOL JEM-2100F) operated at an accelerating voltage of 200 kV.
4.3. Result and Discussions

The preparation of a nanostructured OPV cell based on PCDTBT nanofibers (denoted a “nanofibrous OPV device”) is illustrated in Figure 4.1. First, a thin PCDTBT layer (10 nm) was spin-cast onto a PEDOT:PSS layer as an electron blocking layer. Second, the PCDTBT nanofibers were prepared on the PCDTBT layer by electrospinning a PCDTBT and PEO composite nanofiber (denoted a “PCDTBT@PEO nanofiber”) and selectively removing the auxiliary PEO polymer. PC70BM was subsequently spin-cast onto the top of the PCDTBT nanofibrous layer from a dichloromethane solution (16 mg/mL). Titanium dioxide and aluminum were deposited as the hole blocking layer and cathode, respectively.
Figure 4.1. Schematic diagram showing the preparation of a nanofibrous OPV device.
The diameter of a fiber in an electron donor layer should be sufficiently small that the photogenerated excitons are successfully dissociated. Here, the diameter of a PCDTBT@PEO composite nanofiber was controlled by tuning the conductivity and viscosity of a spinning dope solution, as reported previously (Figure 4.2).
Figure 4.2. SEM micrographs of the electrospun PCDTBT@PEO nanofibers prepared from solutions containing various concentrations of the polar solvents and PEO. The concentrations of PEO were 0.3 wt% (a, d, g), 0.4 wt% (b, e, h), and 0.5 wt% (c, f, i). The chloroform:polar solvent ratios were 10:1 (w/w) (a, b, c), 8:1 (d, e, f), and 6:1 (g, h, i).
Previous efforts toward developing OPV devices using electrospinning techniques have explored the use of P3HT: PC_{60}BM fibers as an active layer\textsuperscript{1} or metal oxide nanofibers as an electron acceptor.\textsuperscript{2, 3} The preparation of an electron donor layer using electrospinning techniques has not yet been investigated because fiber diameters on the scale of the exciton diffusion length had not previously been achieved. The performance of the P3HT: PC_{60}BM fibers in the active layer was not significantly influenced by the fiber diameter because these fibers formed a BHJ structure, the function of which did not significantly depend on the fiber diameter. Metal oxide precursors are readily dissolved in polar solvents with a high electrical conductivity to facilitate the preparation of nanofibers; however, conjugated polymer nanofibers with diameters comparable to the exciton diffusion length cannot be prepared using chlorinated solvents with a low conductivity because the conjugated polymers display a low solubility in such solvents. In chapter 2, a method of preparing P3HT and F8BT nanofibers was suggested.\textsuperscript{4} The viscosity or electric conductivity of the spinning dope solution could be tuned by adding an auxiliary polymer or a polar solvent, respectively. Earlier results indicated that the diameter and morphology of the PCDTBT@PEO nanofibers could be optimized. Since the auxiliary polymer must be removed prior to incorporation into the active layer, the amount of auxiliary polymer added should be minimized as long as beads do not form. Figure 4.2 shows SEM images of the PCDTBT@PEO nanofibers electrospun from different spinning dope solutions. The concentration ratio of the PCDTBT was fixed at 0.1 wt% because the solubility of the PCDTBT was low in this solution. A 0.4 wt% PEO concentration clearly induced the generation of beads on the electrospun fibers. The low viscosity of the 0.4 wt% PEO spinning dope solution (\textbf{Figure 4.3}) was known to be inappropriate for electrospinning, but the highly volatile chloroform appeared to form nanofibers without generating
beads.
Figure 4.3. The viscosities of the spinning dope solutions.
The resultant PCDTBT@PEO composite nanofibers were longer than one centimeter (Figure 4.4(a)), approximately 100 nm in width (Figure 4.4(b)), and did not form beads over a large area. An optical microscopy image (Figure 4.4(c)) and a fluorescence microscopy image (Figure 4.4(d)) revealed that the PCDTBT formed homogeneous fibers in the PCDTBT@PEO composite nanofibers. After selective removal of the auxiliary polymer, the virgin PCDTBT nanofibers that formed the nanoweb displayed diameters of around 20 nm (Figure 4.4(e), (f)), which is an appropriate scale for facilitating exciton dissociation. The small fiber diameter enables the incorporation of PCDTBT nanofibers into the active layer of an OPV device. To the best of our knowledge, the PCDTBT nanofibers are the first electrospun PCDTBT fibers yet reported, and the fiber diameter is the smallest value ever reported for electrospun conjugated polymer fibers. The electrospinning technique permits material savings and large-area fabrication, which are important requirements for OPV device preparation approaches.
Figure 4.4. (a) Electrospun PCDTBT@PEO composite nanofibers with lengths greater than one centimeter. (b) SEM image, (c) optical image, and (d) fluorescence micrographs of the electrospun PCDTBT@PEO composite nanofibers. (e) TEM micrographs of the electrospun virgin PCDTBT nanofibers under low magnification or (f) high magnification.
The removal of the auxiliary polymer was determined by Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA). The strong peaks of PEO are observed in electrospun PEO nanofibers and PCDTBT@PEO composite nanofibers (Figure 4.5). After removal of PEO from the composite nanofibers, characteristic peaks of PEO completely disappeared, indicating that the PEO was successfully eliminated from the composite fibers. The peak located at 795 cm$^{-1}$ is a characteristic peak of PCDTBT, which is not observed in PEO nanofiber sample. In this experiment, four types of virgin PCDTBT nanofibers (average diameters: 20 nm, 50 nm, 120 nm, 200 nm) were prepared (Figure 4.6) by controlling the viscosity and conductivity of the spinning dope solution.
Figure 4.5. FT-IR spectra of electrospun PEO fibers, PCDTBT@PEO composite fibers and PCDTBT virgin fibers.

Figure 4.6. TEM micrographs of the virgin PCDTBT nanofibers with a diameter of (a) 50 nm, and SEM micrographs of virgin PCDTBT nanofibers with diameters of (b) 120 nm, and (c) 200 nm.
The auxiliary polymer was removed from the PCDTBT@PEO composite nanofibers using acetonitrile due to its selective solubility for PEO. Previous reports\textsuperscript{4} indicated that isopropanol displayed the best performance with respect to PEO removal from the composite nanofibers; however, the PEO removal using isopropanol should be performed above 70°C, which can degrade the device. Acetonitrile could dissolve the high molecular weight PEO at room temperature, therefore, acetonitrile was employed in this experiment. The removal efficiency was increased by dipping the layer several times to prevent the re-adsorption of the dissolved auxiliary polymer from the dilute wash solution onto the PCDTBT fibers.\textsuperscript{6}

The residue on the PCDTBT fibers was characterized by FT-IR and TGA. Because PEO fibers were completely degraded at 370°C (\textbf{Figure 4.7}), the PEO residue on the nanofibers could be calculated based on the thermal behavior of the electrospun PEO fibers and the electrosprayed conjugated polymer.\textsuperscript{6} The thermal behaviors of the virgin PCDTBT nanofibers were nearly identical to the behavior of PCDTBT (Figure 4.7), indicating that the PEO was nearly absent from the virgin PCDTBT nanofibers.
Figure 4.7. Thermogravimetric thermograms of the samples under isothermal treatment at 370°C.
The PCDTBT nanofiber diameter was directly related to the concentration of PCDTBT in the electrospinning solution. The electrospun fiber diameter was also influenced by the intensity of the stretching effects during electrospinning, as determined by the electrical conductivity and viscosity of the spinning dope solution. The PCDTBT nanofiber diameter could, therefore, be tuned according to the concentration of PCDTBT, the viscosity, and the electrical conductivity of the spinning dope solution. The effects of the PCDTBT nanofiber diameter on the photovoltaic performance were investigated by preparing four PCDTBT nanofibers with different diameters: 50 nm, 120 nm, and 200 nm. The PCDTBT nanofibers were electrospun from different spinning dope solutions, as illustrated in Figure 4.6.

Previous studies reported that 1-D conjugated polymers display a red-shifted absorption spectrum relative to the bulk spectrum. A red-shifted absorption spectrum is a favorable feature of OPV devices because the materials can absorb a greater number of photons and generate a greater photocurrent. The absorption spectrum of a PCDTBT film showed a peak at 570 nm (Figure 4.8). On the other hand, 20 nm PCDTBT nanofibers displayed a red-shifted peak at 589 nm and higher absorption coefficients at longer wavelengths. Extension and orientation of polymer chain in the fiber during electrospinning process induces a red shift in the absorption peak. The inset of Figure 4.9 shows the selected area electron diffraction (SAED) patterns of PCDTBT film and PCDTBT nanofibers. The diffraction rings in the SAED pattern of PCDTBT nanofibers indicate strain induced crystallization occurred during electrospinning in spite of its amorphous nature. The UV-vis absorption characteristics suggested that the nanofiber-based OPV devices displayed a high photocurrent. Note that a larger red shift was observed in thinner nanofibers. Thicker nanofibers were prepared from the less conductive and highly viscous spinning dope solution, which
did not stretch significantly during the electrospinning process. Differences in the peak
shifts originated from differences in the stretching effects of the various spinning dope
solutions. Clearly, the small-diameter nanofibers offered excellent photon absorption
and exciton dissociation properties.
Figure 4.8. (a) UV-Visible absorption spectra of the PCDTBT nanofibers with different diameters in comparison with the spectrum from a PCDTBT film. (b) Spectra magnified over the range 540–610 nm.
Figure 4.9. TEM micrographs of (a) PCDTBT film and (b) virgin PCDTBT nanofibers. The insets show the SAED patterns of the samples.
Quantitative measurements of the Brunauer–Emmett–Teller (BET) specific surface area of the 20 nm PCDTBT nanofibers, determined by the N₂ adsorption isotherms, indicated a surface area of as high as 71 m²/g (Figure 4.10), much larger than the surface area of the PCDTBT powder (6 m²/g) (Table 4.1).³⁰ The PCDTBT nanofibers displayed a particularly high pore volume, indicating that the thin nanofibers were well-formed. The specific surface area of the PCDTBT nanofibers, 71 m²/g, was almost 5 times the value reported previously for P3HT nanofibers with a diameter of 80 nm (15 m²/g).³⁰ The high surface area of the PCDTBT nanofibers increased the rate of exciton dissociation at the contact area between the PCDTBT and PC70BM materials. The PCDTBT film was assumed to have a specific surface area similar to that of the P3HT film (3 m²/g), which was much lower than the specific surface area of the PCDTBT nanofibers. These results suggested that the nanofibrous OPV device had a much higher interfacial area between the PCDTBT and PC70BM materials than the bilayer OPV device, thereby facilitating photon harvesting and exciton dissociation. As expected, the high BET specific surface area of the PCDTBT nanofibers ensured effective exciton dissociation.
Figure 4.10. N$_2$ adsorption isotherms (at 77 K) for the PCDTBT powders and fibers.
Table 4.1. Specific surface area and pore volume in the materials, characterized according to the N$_2$ adsorption isotherms (at 77K).

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SSA (m$^2$/g)</th>
<th>Total pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDTBT powder</td>
<td>6</td>
<td>0.013</td>
</tr>
<tr>
<td>PCDTBT nanofibers</td>
<td>71</td>
<td>0.300</td>
</tr>
<tr>
<td>P3HT nanofibers$^a$</td>
<td>15</td>
<td>0.014</td>
</tr>
<tr>
<td>P3HT film$^a$</td>
<td>3</td>
<td>-</td>
</tr>
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</table>

$^a$ previously reported value$^{30}$
The active layers of the OPV devices were prepared by coating PC$_{70}$BM onto the PCDTBT nanofibers, and the effects of the nanofiber diameter on exciton dissociation were investigated. Dichloromethane was used as an orthogonal solvent for the conjugated polymers during the fabrication of a bilayer structured$^{32}$ or a nanostructured OPV cell.$^{33-35}$ The solvent selectivity properties were exploited to form a PCDTBT:PC$_{70}$BM heterojunction by spin-coating a solution containing PC$_{70}$BM in dichloromethane onto the PCDTBT nanofibers. The successful formation of a heterojunction and the efficiency of exciton dissociation in the PCDTBT nanofibers were investigated by measuring the photoluminescence (PL) of the PCDTBT:PC$_{70}$BM heterojunction film. A film composed of 20 nm PCDTBT nanofibers almost completely quenched the photoluminescence (Figure 4.11), confirming that the excitons in the PCDTBT nanofibers effectively migrated to the interface of the material and dissociated into electrons and holes.$^{36}$ These results are consistent with previous reports that the domain size should be around 20 nm to facilitate exciton diffusion to the interface.$^{37,38}$ Thicker PCDTBT nanofiber displayed a reduced quenching efficiency in the active layer because the surface area of the thick nanofiber layer was smaller and the exciton migration path was longer.
Figure 4.11. (a) The PL properties of virgin PCDTBT nanofibers with various diameters: PCDTBT nanofibers only (20 nm); active layer composed of PCDTBT nanofibers and PC$_{70}$BM (200 nm, 120 nm, 50 nm, 20 nm). (b) J-V curves for the OPV devices composed of PCDTBT nanofibers with various diameters.
OPV devices are usually fabricated under an inert atmosphere because organic semiconductors can photochemically react with oxidizing agents, such as water vapor and oxygen, thereby degrading the device performance.\textsuperscript{39} Despite the practical merits of air processing, the low performance induced by exposure to air has prohibited the development of air-processed OPV devices. Recently, thermal annealing under vacuum or an inert atmosphere after the deposition of the cathode was found to remove the oxygen atoms incorporated during air processing.\textsuperscript{40,41} In this experiment, I applied a post-annealing step to enhance the performance of the nanofibrous OPV devices processed under ambient air. Because the oxygen atoms extracted during the post-annealing step reacted with the metal cathode to form a metal oxide,\textsuperscript{41} the selection of the cathode or HBL was expected to significantly influence the device performance. Three types of cathode/HBL systems (Al only, LiF/Al, TiO\textsubscript{X}/Al) were prepared on an air-processed BHJ active layer in an effort to identify an optimum system. As shown in \textbf{Figure 4.12}, the TiO\textsubscript{X}/Al cathode system exhibited the best performance. Because a TiO\textsubscript{X} film in an OPV device fabricated under an inert atmosphere is in state of oxygen deficiency (with a Ti:O ratio of 42.1:56.4),\textsuperscript{28} the TiO\textsubscript{X} film offered better extraction of the oxygen from the active layer. Therefore, titanium oxide and aluminum were subsequently deposited onto the active layers to examine the photovoltaic performances of the nanofibers with different diameters. \textbf{Figure 4.11(b)} shows the current density–voltage (J-V) characteristic of the OPV devices prepared from the various active layer types and a TiO\textsubscript{X}/Al cathode system. In conjunction with the PL results, the efficiency and J\textsubscript{SC} of the photovoltaic device increased as the diameter of the PCDTBT nanofibers decreased due to reduced exciton recombination (\textbf{Table 4.2}).
Figure 4.12. Current density–voltage characteristics of an air-processed BHJ OPV device without an interlayer (black line), with a LiF interlayer (red line), and with a TiO$_x$ interlayer (blue line).
**Table 4.2.** Performance details of the OPV devices composed of PCDTBT nanofibers with various diameters.

<table>
<thead>
<tr>
<th>Fiber diameter (nm)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 nm PCDTBT nanofibers</td>
<td>0.851</td>
<td>5.68</td>
<td>35.9</td>
<td>1.74</td>
</tr>
<tr>
<td>120 nm PCDTBT nanofibers</td>
<td>0.846</td>
<td>6.18</td>
<td>38.6</td>
<td>2.02</td>
</tr>
<tr>
<td>50 nm PCDTBT nanofibers</td>
<td>0.843</td>
<td>7.61</td>
<td>43.0</td>
<td>2.76</td>
</tr>
<tr>
<td>20 nm PCDTBT nanofibers</td>
<td>0.860</td>
<td>10.53</td>
<td>48.9</td>
<td>4.43</td>
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</table>
I could further improve the nanofibrous OPV devices by inserting an electron blocking layer between the active layer and the PEDOT:PSS layer to avoid direct contact between the electron acceptor and PEDOT:PSS. Here, the thin PCDTBT layer (10 nm) was spin-cast prior to electrospinning the nanofibers to enhance the selectivity of the charge and performance of the device. The performances of nanofibrous OPV devices were compared with the performances of OPV devices with a conventional structure, i.e., BHJ and pseudo-bilayer devices.

AFM images were acquired to confirm that the active layer surface in the nanofibrous OPV device was smooth (Figure 4.13). Because the nanofibers incorporated into the active layer can induce surface roughness and poor contact with a metal cathode, I obtained AFM images to investigate the surface roughness. The RMS surface roughness in the nanofibrous OPV device (1.93 nm) was slightly higher than that observed in the BHJ (1.42 nm) or pseudo-bilayer (1.19 nm) devices but the roughness was still comparable to the values reported previously for spin-cast films. Therefore, I concluded that the nanofibrous film had an appropriate surface for use in OPV devices.
Figure 4.13. AFM images (2 μm x 2 μm) of the (a) BHJ, (b) pseudo-bilayer, and (c) nanofibrous active layers composed of PCDTBT:PC₇₀BM.
The photovoltaic characteristics of the BHJ, pseudo-bilayer, and nanofibrous OPV devices are summarized in Table 4.3, and the corresponding J-V curves are illustrated in Figure 4.14(a). As reported earlier, the pseudo-bilayer structured OPV device displayed a low JSC (3.82 mA/cm²) because the low specific surface area of the pseudo-bilayer film compromised the exciton diffusion and light absorption properties. The reference BHJ OPV devices exhibited an open-circuit voltage (VOC) of 0.917 V, JSC of 9.95 mA/cm², and a fill factor (FF) of 59.3%, and a power conversion efficiency (PCE) of 5.41%. The enhanced JSC resulted from the effective harvesting of excitons. A comparison to the performances of the nanofibrous OPV devices clearly revealed that the JSC of the nanofibrous device was even higher, 11.54 mA/cm², than the value of the BHJ OPV device. The enhanced JSC in the nanofibrous OPV device was almost 3 times the JSC value in the pseudo-bilayer OPV device and 115% of the JSC value observed in the BHJ OPV device. Although the high series resistance yielded a relatively low FF (56.4%) for the nanofibrous OPV device, the high JSC provided a total PCE (5.82%) that was higher than the value of the BHJ OPV device. The high series resistance originated from the high bulk resistance of active layer and contact resistance between layers. The low fill factor in the nanofibrous OPV devices may have been caused by damage incurred during the removal of the auxiliary polymer and the long exposure time in ambient air. Likewise, the low VOC in the nanofibrous OPV devices would have been caused by the defects and traps induced through the exposure in air and small amount of residual auxiliary polymer. Additional improvement in the performance could potentially be made by developing better processing techniques.
**Table 4.3.** Performance details of the BHJ, pseudo-bilayer, and nanofibrous structured OPV devices.

<table>
<thead>
<tr>
<th></th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$J_{SC}$ (mA/cm²) (from IPCE)</th>
<th>Hole mobility (cm²/Vs)</th>
<th>Series resistance (Ω/cm²)</th>
<th>Shunt resistance (Ω/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHJ OPV device</td>
<td>0.917</td>
<td>9.95</td>
<td>59.3</td>
<td>5.41</td>
<td>9.98</td>
<td>4.68×10⁻⁵</td>
<td>15.1</td>
<td>520.9</td>
</tr>
<tr>
<td>(0.913±0.006)</td>
<td>(9.71±0.37)</td>
<td>(58.2±1.2)</td>
<td>(5.16±0.19)</td>
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<tr>
<td>Pseudo-Bilayer OPV device</td>
<td>0.916</td>
<td>3.82</td>
<td>60.2</td>
<td>2.11</td>
<td>4.01</td>
<td>3.59×10⁻⁵</td>
<td>36.8</td>
<td>1399.6</td>
</tr>
<tr>
<td>(0.914±0.003)</td>
<td>(3.71±0.11)</td>
<td>(59.2±0.7)</td>
<td>(2.01±0.07)</td>
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<tr>
<td>Nanofibrous OPV device</td>
<td>0.894</td>
<td>11.54</td>
<td>56.4</td>
<td>5.82</td>
<td>11.45</td>
<td>4.24×10⁻⁵</td>
<td>22.2</td>
<td>533.9</td>
</tr>
<tr>
<td>(0.894±0.002)</td>
<td>(11.38±0.12)</td>
<td>(55.9±1.3)</td>
<td>(5.69±0.15)</td>
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* Numbers in parentheses indicate average values
Figure 4.14. (a) J-V curves and (b) IPCE spectra of the devices prepared using the PCDTBT:PC$_{70}$BM BHJ, pseudo-bilayer, and nanofibrous structures.
Figure 4.15. Device performance variation on the exposure time in ambient air.
Park et al. reported that the photocurrent of their OPV device flattened under reverse bias conditions because the internal quantum efficiency of the OPV device approached 100%. These results indicate that the OPV device had extracted the photogenerated charge under short circuit conditions. Consequently, no additional charges could be harvested, even under high reverse bias conditions. In view of these results, I tested our BHJ/pseudo-bilayer/nanofibrous OPV devices under reverse bias conditions to determine whether the nanofibers affected the charge collection. The photocurrent was obtained by subtracting the dark current from the light current to compensate for the diode. All three types of OPV devices showed flatter current densities below 0 V, but the current density slope for the nanofibrous OPV device was smaller than the slope for the BHJ device.
Figure 4.16. Calculated photocurrent density–voltage curves of the devices prepared using the PCDTBT:PC$_{70}$BM BHJ, pseudo-bilayer, and nanofibrous structures.
Given that the hole mobility is usually lower than the electron mobility in an OPV device, the hole mobility of a device can significantly influence the balance between the electron and hole mobility. The hole mobility of the devices was determined using a space charge limited current (SCLC) model for the behavior of the electronic charge in the organic semiconductor at low applied voltages. The hole transport in OPV devices processed in both N₂-processed and air-processed could be described according to the SCLC model, as the square root of dark current increased linearly with the bias voltage in a hole-only device. The SCLC model predicted the relationship between the current and bias voltage using the Mott–Gurney square law,

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}, \quad (1)$$

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative dielectric constant, $\mu$ is the mobility in the semiconducting polymer, $V$ is the effective applied voltage, and $d$ is the thickness of the film. **Figure 4.17** shows the $J^{1/2}$-$V$ curves for each device, and all devices showed a linear relationship and were well-described by the Mott–Gurney square law. The hole mobility of the BHJ OPV device was $4.68 \times 10^{-5}$ cm²V⁻¹s⁻¹, which was comparable to the value reported previously for a PCDTBT:PC₇₀BM OPV device. Despite the use of air-exposed processing, the hole mobility of the BHJ OPV device in this experiment was not significantly degraded. These results indicated that the brief air exposure did not considerably influence the performance. The hole mobility of the nanofibrous OPV device was found to be $4.24 \times 10^{-5}$ cm²V⁻¹s⁻¹. This value was comparable to the values obtained for the BHJ ($4.68 \times 10^{-5}$ cm²V⁻¹s⁻¹) and pseudo-bilayer ($3.59 \times 10^{-5}$ cm²V⁻¹s⁻¹) OPV devices, despite the presence of possible damage or long exposure to air, possibly due to the better electrical properties of the 1-D materials.
Figure 4.17. Dark $J^{1/2}$-V characteristics for the SCLC hole-only devices prepared using the PCDTBT:PC$_{70}$BM BHJ, pseudo-bilayer, and nanofibrous structures.
The effects of the red-shifted absorption on the photovoltaic performance were further investigated by measuring the incident photon-to-current efficiency (IPCE) of each OPV device. The $J_{SC}$ values calculated from the IPCE data and the J-V curve were in good agreement (Table 4.3). The IPCE of the nanofibrous device exceeded the value of the BHJ and pseudo-bilayer device, especially in the long-wavelength region (Figure 4.14(b)). It should be noted that the nanofibrous device harvested low-energy photons more effectively than the BHJ device, as revealed by the UV-vis absorption characteristics. These results indicated that the light absorption, exciton dissociation, and charge transport were effectively enhanced in the nanofibrous device, thereby improving the $J_{SC}$ for a nanofibrous OPV device compared with the BHJ and pseudo-bilayer devices.

The nanomorphology of the BHJ, pseudo-bilayer, and nanofibrous devices were investigated with cross-sectional TEM (Figure 4.18). Defocused TEM images and bright TEM image were presented to see the phase contrast and interface of the device, respectively. The defocused TEM image reveals the pseudo-bilayer device has two distinct regions; PCDTBT:PC$_{70}$BM mixture region and pure PC$_{70}$BM region. The top region is slightly darker than bottom, indicating that the top region is composed of pure PC$_{70}$BM. On the other hand, BHJ device and nanofibrous device had no interface. This means that spin-casting of the PC$_{70}$BM film into the nanofibers successfully formed an intermixed layer as BHJ device formed.
Figure 4.18. Cross-sectional TEM defocused (~ -10 μm defocused) phase contrast images of (a) BHJ device (b) pseudo-bilayer device and (c) nanofibrous device (Scale bar: 50 nm). (d) Cross-sectional TEM bright image of BHJ device.
4.4 Conclusions

In summary, PCDTBT nanofibers with diameters below 20 nm were successfully prepared using an electrospinning method. The high aspect ratio, high surface area, and small domain sizes of the nanofibers provided a favorable morphology for the active materials of an OPV device. Nearly 100% PL quenching and a higher $J_{SC}$ in the nanofibrous OPV devices indicated effective charge transport and exciton dissociation in the device. This preparation method may be extended to other conjugated polymers for the preparation of large-area nanofibers and nanofibrous OPV devices under ambient conditions.
4.5. References

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Part III

Design and Performance of a Carbon-Nanomaterial-Based Encapsulation Layer and Electrodes for Flexible Photovoltaic Devices
Chapter 5. Preparation and Characterization of Reduced Graphene Oxide Based Encapsulation Film

5.1. Introduction

OPV devices are viewed as a potential next-generation photovoltaic device due to easy solution process, lightweight, and flexibility.\(^1\)\(^,\)\(^2\) However, short lifetime of the OPV devices prevents it from being main photovoltaic device in the field.\(^3\)\(^,\)\(^4\) Low stability of the OPV devices is induced from several reasons, such as morphology change in active layer\(^5\) and degradation of PEDOT:PSS and electrode.\(^6\) However, the main reason of the low stability is induced from chemical oxidation in active materials.\(^4\)\(^,\)\(^7\)\(^,\)\(^8\) Conjugated polymers are easily oxidized in presence of oxidizing agent and light, leading to the degradation of the organic electronic device.\(^7\) OPV devices should be encapsulated to avoid performance degradations caused by the oxidizing agent, especially water vapor in an ambient atmosphere. Encapsulation of an organic device with glass attached using epoxy resin is a straightforward means of protecting against water vapor on a laboratory scale. A very low WVTR of the glass (< \(10^{-6}\) g/m\(^2\) day) sufficient to satisfy the requirements of an organic light-emitting device, a commercialized organic electronic device, is necessary.\(^9\) However, this method is fundamentally unsuitable for flexible devices due to the brittleness of the glass. PEN has attracted much interest as an alternative to glass substrates due to its high strength, high modulus, good chemical resistivity, good thermal resistivity, and feasible gas barrier properties. The WVTR of PEN, however, is 3 g/m\(^2\) day, which is higher than necessary (\(10^{-4}\) g/m\(^2\) day) to ensure a sufficient lifetime of OPV devices. Therefore, a flexible encapsulation system is required to prepare flexible organic electronic devices.
Graphene has recently attracted much attention due to its high specific surface area, useful mechanical properties, and gas impermeability. Because small gas molecules including helium cannot pass through a graphene layer, graphene is a good candidate as a gas barrier film for organic electronic devices. Among the synthetic routes recently proposed to prepare graphene, chemical exfoliation of graphite with a subsequent reduction step allows for solution-processing and up-scaling. Graphene oxide (GO) is a chemically exfoliated graphite layer containing many epoxide, hydroxyl, ketone, and carboxyl groups on the surface. It has high dispersibility in polar solvents and forms a stable colloidal solution that can be used in solution-processing. GO is quite different from graphene due to its many functional groups, but it is easily reduced by a heat treatment or by chemical reagents into reduced GO (rGO). The rGO has higher electrical property and a more hydrophobic surface, as the oxygen-containing groups are mostly removed during the reduction step.

In this work, I demonstrate how simply and directly prepared rGO films on OPV devices enhance the stability of the devices in ambient air. The WVTR of rGO films prepared on flexible substrates can be enhanced by controlling the reduction condition. The dispersibility of the GO is significantly influenced by the starting graphite materials and dispersion method. GO solution obtained from flake graphite, specifically a horn-type sonicated solution, shows high dispersibility, leading to good gas barrier performance of rGO film. The slow heating rate during the thermal reduction process on GO film results in low surface roughness, a small BET specific surface area, and a low WVTR value.
5.2. Experimental

5.2.1. Preparation of the GO solution

GO was prepared by a modified Hummer’s method from small-size powder graphite (Sigma Aldrich), medium-size flake graphite (Bay Carbon), and large-size flake graphite (Sigma Aldrich) (denoted as GO(S), GO(M), and GO(L), respectively). The solvent of the as-prepared GO aqueous suspension was changed to isopropanol (IPA) by repeated centrifugation and resuspension in IPA. The GO(L) suspension was sonicated for 30 min to enhance the dispersion. The small-sized GO in the sonicated suspension was removed by centrifugation of 10,000 rpm for 30 min (denoted as GO(L, sonic)).

5.2.2. Fabrication and characterization of OPV devices

ITO/glass substrates were cleaned by sonication in a detergent and in acetone and IPA. The ITO substrates were then treated by UV/ozone for 15 min. To fabricate OPV devices with a normal structure, PEDOT:PSS (Clevios P VP Al 4083, H.C. Stark) was spin-cast at 5000 rpm for 40 s. The PEDOT:PSS films were dried at 150 °C for 15 min and then transferred into a glovebox filled with argon. Active layers were spin-cast from a solution of P3HT:PC_{60}BM (1:0.8 w/w) in o-dichlorobenzene at 800 rpm for 30 s. The devices were completed by the thermal evaporation of a 100 nm Al cathode. To fabricate PCDTBT:PC_{70}BM devices, 4 mg of PCDTBT and 16 mg of PC_{70}BM were dissolved in 1 ml of chlorobenzene. The solution was spin-cast onto the PEDOT:PSS layer at 2000 rpm for 40 s. 10 nm TiO_{x} and 100 nm Al were then deposited by thermal evaporation. The power conversion efficiency (PCE) of the devices was determined
using a K3000 instrument (McScience). To examine the stability of the OPV devices, the devices were stored in ambient air (25 °C, relative humidity: 40 %) under illumination.

5.2.3. Preparation and characterization of the rGO film

The GO suspension was repeatedly spin-cast onto an aluminum electrode at 2000 rpm. To obtain rGO film, the encapsulated OPV device was heat-treated at 150 °C for 30 min. PEN/rGO films were obtained by spraying the GO(L, sonic) suspension with a subsequent heat treatment. RGO(L, SONIC)_01C and rGO(L, sonic)_10C were heated to 200 °C at heating rates of 0.1 °C/min and 10 °C/min, respectively.

5.2.4. Fabrication of a flexible OPV device

The GO(L, sonic) suspension and a poly (methyl methacrylate) (PMMA) solution were mixed, with the weight ratio of the GO(L, sonic) and PMMA solutions being 1:100. This solution was sprayed onto a PEN film to prepare a transparent gas barrier film. 1 mg of SWCNT (Timesnano) in 0.95 ml of PEDOT:PSS (Clevios PH1000, H.C. Stark) and 0.05 ml of a dimethyl sulfoxide suspension were sonicated for 3 hours in an ice bath. Unwrapped SWCNTs were removed by centrifugation at 13,000 rpm for 30 min. The supernatant solution was spin-cast onto the PEN/GO film at 5000 rpm for 40 s. The film then underwent a thermal treatment at 150 °C for 30 min. The fabrication processes of the other layers, including the active layer, TiOₓ, Al, and the gas barrier layer, were identical to those used during the preparation of the solar cell.
5.3. Results and discussion

5.3.1. Direct preparation of rGO films on OPV devices for encapsulation

To prepare rGO film on the OPV device directly from the GO solution, damage to the OPV device during the processing of the GO layer should be avoided. Therefore, chlorinated solvents as well as water are excluded as candidates. In addition, other polar solvents such as DMF, dimethyl sulfoxide, and acetone also degrade OPV devices (Figure 5.1). Alcohols have been used to spin-cast a hole blocking layer or as a solvent treatment of the active layer. Treatment by alcohols on aluminum did not influence the performance of the OPV device, indicating that alcohols are suitable solvents for solvent-processing on aluminum directly.
Figure 5.1. J-V curves of P3HT:PC_{60}BM devices treated by solvents.
The physical and chemical properties of GO differ from those of the raw materials. Many types of graphite, including flake and powder types, have been used to prepare GO by chemical exfoliation. I prepared GO through exfoliation from small-size powder graphite, medium-sized powder graphite, and flake graphite. The lateral size of the GO(L) is larger than tens of micrometers, which is the largest value among the prepared GOs (Figure 5.2). Given that the flake graphite is larger than the other type of powder graphite, this is a fairly intuitive result. To prepare GO or rGO films directly on the OPV devices by spin-casting, GO solutions are necessary. An aqueous solution cannot be used to preserve the stability of the OPV device; thus, IPA was chosen for spin-casting.
Figure 5.2. SEM micrographs of the (a) GO(S), (b) GO(M), and (c) GO(L).
The dispersion of nanocarbons has been thoroughly and extensively studied due to the aggregation behavior of nanocarbons. In spite of the high dispersibility of GO in water due to the functional groups on its surface, dispersion in other organic solvents such as alcohols is known to be poor. A well-dispersed solution is necessary for solution-processing. All GO samples were dispersed in IPA to prepare the GO solution for spin-casting onto OPV devices directly. **Figure 5.3** shows the dispersion stability of the each GO sample in IPA. Due to the size of the raw materials, it is expected that GO(L) is largest among the GOs, leading to poor dispersion. However, note that the GO(L) is well dispersed in IPA compared to GO(S) and GO(M). In contrast to GO(L), GO(S) and GO(M) are not stable for a long time in IPA.
Figure 5.3. Images of (a) GO(S), GO(M), and GO(L) dispersed in IPA after vigorous stirring and (b) after stirring for 1 day.
I prepared the GO and rGO layer on the aluminum of the OPV device by the spin-casting of the GO solution. The rGO layer was obtained after thermal annealing at 150 °C for 30 min, which is a conventional thermal treatment for P3HT:PC₆₀BM devices. The stability levels of the devices were characterized, as shown in Figure 5.4. The PCE of the reference sample, which is not encapsulated, is dramatically decreased. After 6 hours in ambient air, the PCE was close to 0. This result demonstrates the poor stability of P3HT:PC₆₀BM device in ambient air with light. Interestingly, the devices covered with GO film did not show enhanced stability, indicating that the GO layer did not protect against water vapor. This result is consistent with an earlier result reported by Geim et al.,¹² who showed that the water permeability of GO film is similar to that of an open aperture. On the other hand, the rGO-covered OPV device exhibited enhanced stability. The simple heat treatment, which should be performed to obtain high efficiency in P3HT:PC₆₀BM devices, increased the gas barrier property remarkably. Compared to the reference device, the stability was enhanced by nearly 25 times after the addition of the rGO(L) layer on top of the OPV devices.
Figure 5.4. Comparison of the cell performance under an ambient condition for cells without encapsulation and with GO and rGO encapsulation.
Despite the high dispersion stability of GO(L) in IPA, aggregation was observed after 1 month (Figure 5.5(a)). Sonication is broadly used to disperse nanocarbons such as CNTs, GO, and rGO. The dispersion stability of GO(L) was highly enhanced after 30 min of sonication (denoted as GO(L, sonic)), and it remained in a dispersion state after 1 month (Figure 5.5 (b)). However, it is known that sonication breaks GO into GO of a smaller size. Indeed, the GO(L) in this experiment before sonication has a lateral size on the scale of tens of micrometers, but lateral size of the GO(L, sonic) was decreased to around 1 micrometer (Figure 5.5. (c, d)).
Figure 5.5. Images of (a) GO(L) and GO(L, sonic) dispersed in IPA and (b) 1 month after dispersion. SEM images of (c) the GO(L) and (d) GO(L, sonic) samples.
The gas barrier performance of rGO(L, sonic)-based film is higher than that of rGO(L) (Figure 5.6). The OPV devices encapsulated by rGO(L, sonic) film showed only 5% reduction in PCE after 3 hours, which showed high stability compared with the reference devices. Only one additional process between the evaporation process and the thermal annealing step improved the stability significantly. The result indicates that high dispersibility induced by sonication increases the performance of the gas barrier film despite the reduction of the lateral size of the single GO. The low specific surface area of the rGO(L, sonic) sample also supports the high gas barrier performance. Because relatively small materials usually have a high specific surface area (SSA), it is expected that rGO(L, sonic) has a larger SSA than rGO(L) due to the smaller lateral size of rGO(L, sonic). However, the SSA of GO(L, sonic) is smaller than that of GO(L) (Table 5.1). The SSA of unsonicated GO was 6.8 m²/g, whereas GO(L, sonic) has a SSA of 4.05 m²/g. A low BET SSA means that the surface area that adsorbs the gas molecules is small, indicating that the gas molecules cannot easily permeate the surface. The difference between rGO(L) and rGO(L, sonic) can be found in microscopy images. RGO(L) has very large lateral size, but many wrinkles exist on the surface of rGO(L) (Figure 5.7). On the other hand, the rGO(L, sonic) sample has a very smooth surface despite its small lateral size. This series of results is correlated with the XRD data. The 2θ value of GO(L) is 9.54°, corresponding to an interlayer distance of the 9.26 Å, which is larger than the interlayer distance of GO(L, sonic) (8.41 Å) (Figure 5.8). These results suggest that the gas barrier property of rGO film depends on the prevention of the infiltration of gas molecules by the stacking of rGO layers rather than on the lateral size of the rGO film. This direct spin-casting process on the OPV device realizes mid-term stability, and I expect that longer stability of the device can be achieved with the proper control of the physical and chemical properties of GO.
Table 5.1. BET SSA and pore volume in the materials, characterized according to the N\textsubscript{2} adsorption isotherms (at 77K)

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SSA (m\textsuperscript{2}/g)</th>
<th>Total pore volume (cm\textsuperscript{3}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO(L)\textsuperscript{a}</td>
<td>6.8</td>
<td>0.007</td>
</tr>
<tr>
<td>GO(L, sonic)</td>
<td>4.1</td>
<td>0.004</td>
</tr>
<tr>
<td>rGO(L)_05C\textsuperscript{a}</td>
<td>7.6</td>
<td>0.015</td>
</tr>
<tr>
<td>rGO(L)_20C\textsuperscript{a}</td>
<td>13</td>
<td>0.023</td>
</tr>
<tr>
<td>rGO(L, sonic)_01C</td>
<td>5.9</td>
<td>0.006</td>
</tr>
<tr>
<td>rGO(L, sonic)_10C</td>
<td>6.8</td>
<td>0.008</td>
</tr>
</tbody>
</table>

\textsuperscript{a} previous reported value\textsuperscript{17}
Figure 5.6. Stability of the cell performance under an ambient condition for cells without encapsulation and with rGO(L) films.
Figure 5.7. AFM images of (a) the GO(L) and (b) GO(L, sonic) samples.

Figure 5.8. XRD patterns of GO(L) and GO(L, sonic) samples.
5.3.2. Preparation of flexible rGO-based encapsulation films

Compared to direct spin-casting on the device, GO film cast onto PEN film involves fewer limitations in terms of the reduction method used. Many chemical, thermal and optical methods have been suggested to reduce GO film or powder. The typical method of GO reduction is chemical reaction with GO and a reducing agent such as NaBH₄. However, the GO film on the PEN here became detached from the substrate during the reduction process by NaBH₄ (Figure 5.9). The conventional chemical reduction method is inappropriate for fabrication of rGO-based gas barrier film on a substrate.
Figure 5.9. Images of (a) GO film on PEN substrates, (b) after dipping in NaBH$_4$ solution for 2 hours at 80 °C, and (c) after thermal annealing at 200 °C.
The low-temperature thermal treatment performed below 170 °C is compatible with the flexible substrate PEN. Contrast to the chemical reduction method, thermal annealing enables the reduction without the detachment and/or damage of the GO film. During the low-temperature thermal reduction process, the heating rate influences the porosity and structure of the rGO, which may influence the gas barrier performance. Figure 5. 10 shows the images of flexible and freestanding GO and rGO films. Both rGO(L, sonic)_{10C} film (Heating rate: 10 °C/min) and rGO(L, sonic)_{01C} film (Heating rate: 0.1 °C/min) were well reduced and sustained flexibility, but the surface morphology of the films was different. RGO(L, sonic)_{10C} film has very rough surface. High heating rate would induce the bumpy morphology of the sample. OM images also indicate the bumpy and smooth surface of the rGO(L, sonic)_{10C} and rGO(L, sonic)_{01C} film, respectively.
Figure 5.10. Picture (a, b, c) and optical microscopy image (d, e, f) of the (a, d) GO(L, sonic), (b, e) rGO(L, sonic)_10C and (c, f) rGO(L, sonic)_01C samples.
The high roughness of the film was also observed in microstructure. The surface roughness quantitatively characterized by AFM of the rGO(L, sonic)_10C samples is 4.7 nm, which is higher than that of rGO(L, sonic)_01C (3.5 nm) (Figure 5.11). This microstructural change will influence the gas permeation and SSA. The BET SSA of the GO(L, sonic) increased by 85.4% and 65.8% after reduction at a heating rate of 10 °C/min and 0.1 °C/min, respectively (Table 5.1). A high heating rate induced a more porous structure and a high BET SSA. Note that the rGO(L, sonic) samples showed low BET SSA compared with rGO(L) samples. Reduction of size and wrinkles on the surface by sonication induces the small SSA, as observed in GO(L) and GO(L, sonic) films.
Figure 5.11. AFM images of (a) GO(L, sonic), rGO(L, sonic)_10C and (b) rGO(L, sonic)_01C.
SAXS was employed to further confirm the evolution of a textured structure as a function of the heating rate. The “fractal dimension D” of a fractal object generally represents the “openness” of the object in terms of self-similar branches at a certain length. The fractal objects obey a power law scattering, and the fractal dimensions can be calculated by obtaining the slope of a log-log plot of the intensity as a function of the scattering vector $q$, where $q = 4\pi\lambda^{-1}\sin(h)$, with $2h$ and $k$ being the scattering angle and the incident X-ray wavelength, respectively (Figure 5.12). The fractal dimension of GO(S) and rGO(S)_01C were determined to be 2.14 and 2.35, respectively, implying that the fractal dimensions of GO and rGO(S)_01C followed the mass fractal dimension ($1 < D < 3$). The mass fractal dimensions indicated that the GO and rGO(S)_01C were composed of two-dimensional sheets that interacted. For the case of rGO(S)_10C, the fractal dimension was 3.26, indicating that this material displayed a surface fractal dimension ($3 < D < 4$). Thus, the 3.26 value revealed that rGO(S)_01C was a three-dimensional structure with a fractally rough surface.
Figure 5.12. SAXS curves of the products.
Regardless of the heating rate, a peak from the expanded interlayer distance of GO (Figure 5.8) was shifted such that it was close to 24°. Figure 5.13 shows the XPS results and quantitative analysis results of the various films. The peaks in the C1s spectra of the GO and rGO samples were assigned to the C=C (284.4 eV), C–C (289.5 eV), C–O (286.2 eV), C=O (287.2 eV), and O–C=O (288.5 eV) modes.\textsuperscript{10, 17} XPS results also show the oxygen functional groups on the surface of the GO were decreased after the reduction process. It is noticeable that the heating rate significantly influences the surface morphology, SSA, microstructure of rGO films without variation of reduction state and degree.
Figure 5.13. C1s XPS spectra of the GO and rGO films.
Table 5.2 lists the WVTR value according to a MOCON instrument. The as-prepared PEN film shows a value of 2.67 g/m² day. In contrast to the small reduction of WVTR in rGO film prepared without sonication, the WVTR value of the rGO(L, sonic)₉₀C film decreased by one order of magnitude. Despite the thin thickness of the rGO film (10 nm) compared with the PEN film (100 μm), the gas barrier performance was higher. The WVTR value of rGO(L, sonic)₉₁C was even smaller due to the smaller BET SSA and surface roughness. The WVTR value of the rGO(L, sonic)₉₁C sample is only 0.05 g/m² day, which is only 2% of that of the as-prepared PEN film.
Table 5.2. WVTR value of PEN and PEN/rGO films as characterized by the MOCON instrument

<table>
<thead>
<tr>
<th>Samples</th>
<th>WVTR (g/m²day)</th>
</tr>
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<tbody>
<tr>
<td>PEN</td>
<td>2.67</td>
</tr>
<tr>
<td>GO(L)</td>
<td>2.54</td>
</tr>
<tr>
<td>rGO(L)</td>
<td>1.70</td>
</tr>
<tr>
<td>rGO(L, sonic)_10C</td>
<td>0.214</td>
</tr>
<tr>
<td>rGO(L, sonic)_01C</td>
<td>0.047</td>
</tr>
</tbody>
</table>
PCDTBT is known as a stable material with high power conversion efficiency. Also, cathode buffer layer consisting of TiO$_x$ in a PCDTBT-based OPV device increases the stability in air by blocking oxidizing agent. Indeed, it takes 240 hours to decrease the efficiency to 50% in ambient air (Figure 5.14(a)), which shows high stability of PCDTBT:PC$_{70}$BM cell compared with P3HT:PC$_{60}$BM cell. Lifetime of the PCDTBT-based OPV device would be more enhanced by encapsulation of the device. However, direct encapsulation method is incompatible with the PCDTBT:PC$_{70}$BM device because thermal treatment at 150 °C decreases the efficiency of the PCDTBT-based device. Therefore, PCDTBT:PC$_{70}$BM device should be encapsulated by the gas barrier film and glue system. Here, the devices were tested at a relative humidity level of 100%. In this condition, the efficiency of the PCDTBT:PC$_{70}$BM cell decreased to 7% after 24 hours (Figure 5.14(b)). The efficiency drop was much faster compared to that in the ambient condition, as this is a fairly harsh condition. The OPV device encapsulated by the rGO(L, sonic)$_{10}$C and rGO(L, sonic)$_{01}$C film showed a value of 13%, 43% after 240 hours, respectively. This is highly enhanced stability compared to the OPV device encapsulated by the as-prepared PEN film.
Figure 5.14. Efficiency variation of PCDTBT:PC_{70}BM inverted OPV devices encapsulated by PEN/rGO film stored at (a) ambient air and (b) 100% relative humidity.
To fabricate a flexible solar cell, flexible transparent conducting film (TCF) was prepared on a PEN substrate. Because the substrate was changed from glass to PEN, the gas barrier film had to be on the TCF side. The gas barrier film should also be transparent when using gas barrier film on the TCF side. To enhance the transparency of the gas barrier film, the amount of rGO should be reduced. Here, a GO-polymer composite was cast to protect against water vapor and to increase the transparency. The gas barrier property of the polymer composite is determined by the following equation, as proposed by Gusev and Lusti,

$$\frac{P}{P_m} = \frac{1 - \phi}{(1 + A_f \phi / 3)^2},$$

where $P$ is permeability of the composite, $P_m$ is the permeability of the matrix, $\phi$ is the volume ratio, and $A_f$ is the aspect ratio. According to the equation, a material with a high aspect ratio, such as graphene, will show excellent performance.

PMMA/rGO composite film was prepared to achieve both gas barrier properties and transparency in this experiment. The transmittance at 550 nm of the composite film was 95%, and the WVTR value was 0.18 g/m² day, which is similar to those values of rGO film.

The flexible TCF was prepared by the spin-casting of a SWCNT/PEDOT:PSS solution. The dispersion of SWCNT has been an issue preventing its wider use in electronic devices. Common dispersion methods for CNTs are 1) the adsorption of a surfactant on the surface, 2) wrapping of polymer on the surface, and 3) surface functionalization by an acid treatment. However, the insulating properties of the surfactant and polymer prevent the conductivity from increasing, and the acid treatment generates defects on the surface. Here, PEDOT:PSS, which is one of the most conductive polymers, wrap the surface of SWCNTs to disperse them in an aqueous solution. PEDOT:PSS acts as
both a wrapping agent and a composite matrix; therefore, the SWCNTs are wrapped and dispersed in the PEDOT:PSS solution. Furthermore, the work function of the composite film is suitable for OPV devices due to the PEDOT:PSS. The surface resistance and transmittance at 550 nm are 200 Ω/sq and 90%, respectively.

**Figure 5.15** shows a flexible device based on the gas barriers and the TCF. The structure of the device was as follows: PEN substrate/PMMA:rGO gas barrier film/SWCNT:PEDOT:PSS TCF/PCDTBT:PC_{70}BM active layer/TiO_{x}/Al. The J-V curves are illustrated in **Figure 5.16**. The flexible device has a J_{SC} value of 6.05 mA/cm^2, a V_{OC} value of 0.883 V, an FF value of 39.6%, and a PCE value of 2.11%. The bending stability of the devices was characterized by their radius of curvature of 1 cm. The efficiency was decreased by about 9% after bending the devices 40 times (**Figure 5.17**), mainly due to the degraded J_{SC} and FF values.
Figure 5.15. Image of a flexible OPV device based on the flexible TCF and gas barrier film.

Figure 5.16. J-V curves of the flexible devices.
Figure 5.17. Normalized photovoltaic parameter as a function of the number of bending cycles.
Finally, the stability of the devices was characterized. The efficiency of the device after 2 days at 100% RH was 1.30%, which is the 62% of that of the as-fabricated device (Figure 5.16). Therefore, this device has both good flexibility and stability simultaneously.
5.4. Conclusion

RGO-based gas barrier film was prepared by solution-processing for flexible devices. The flexible devices showed good efficiency and stability. Further work on the remaining issues pertaining to the rGO films, including reductions, the matrix, and multiple layers will lead to enhanced performance and stability of flexible OPV devices.
5.5. Reference

Chapter 6. Concluding remarks

Solar cells are capable of converting solar energy into electrical energy, and act as future-oriented power generation devices of renewable energy. Some developments are required for solar cells due to the high costs involved and inadequacy in flexible devices. These problems can be resolved by OPVs based on solution-processable conjugated polymers, but such materials are accompanied by issues in efficiency, lifespan, and the flexibility of various components such as substrate, electrode, and encapsulation film.

This thesis addressed the above issues and developed flexible solar cells having high efficiency and long lifespan. The active layer, while using conjugated polymer, achieved better performance through morphology control instead of synthesis with new materials. Conjugated polymer nanofibers with a 20 nm diameter, two times the exciton diffusion length, were successfully obtained by electrospinning. This enabled the development of high-efficiency OPVs. Graphene was used for successful encapsulation of OPV, allowing a longer lifespan while maintaining flexibility and solution processing. By replacing electrode materials with CNT, a flexible OPV in the structure of CNT electrode/conjugated polymer active layer/graphene encapsulation was formed.

In this study, there are two issues that have only been partially resolved and left to be dealt with in future work. The first issue is related to fabrication technique, that is, the potential of electrospinning for large area and continuous processing. Electrospinning is a method that can be included in the roll-to-roll process, and thus suitable not only for morphology control, but also for large area and continuous processing. By
combining electrospinning with the electrospray method, the entire process can be realized in the form of continuous processing if electrospray replaces spin-casting in the stacking of other layers.

Another issue yet to be fully resolved is the development of all-carbon solar cells. Since materials from the electrode to encapsulation involve sp2 carbon, every solar cell component can be made from carbon-based materials if the cathode is replaced. This may be possible by tuning of graphene, used as an encapsulation film in this study, to serve the dual function of cathode and encapsulation film. It will be possible to produce all-nanocarbon solar cells by replacing conjugated polymer in the active layer with carbon nanomaterials. This is expected to lead to the production of solar cells that fundamentally resolve lifespan and stability issues.

The theoretical background and experimental results of this thesis show that performance is significantly affected by the preparation and processing of adequate materials for each component. Further advancements in high-efficiency, long-lasting, and flexible solar cells will be achieved through in-depth theoretical examination, introduction of new materials, and development of adequate processing techniques.
요약 (국문 초록)

이 연구는 \( sp^2 \) 탄소재료를 기반으로 한 높은 광변환 성능과 장시간의 안정성을 가지는 유연성 태양전지의 설계와 그 성능 분석에 관한 것이다. 태양전지는 신재생에너지인 태양에너지를 전기에너지로 변환하는 차세대 에너지 전환 기기이다. 유기 태양전지는 나노탄소와 공액 고분자들과 같은 \( sp^2 \) 탄소를 기반으로 하여 구성되는 태양전지로 용액공정을 통한 높은 생산성과 낮은 가격, 유연성으로 대표되는 장점으로 인해 기존 태양전지의 단점을 극복할 수 있는 차세대 태양전지로 여겨진다. 그러나 유기 태양전지는 낮은 효율과 안정성에 관련된 문제는 상용화를 위해서 해결되어야 할 이슈로, 이를 극복하기 위해 최근들어 여러 그룹에서 연구가 진행되고 있다. 본 연구에서는 해당 이슈를 해결하기 위해 먼저 이론적 고찰을 시도하여 효율과 수명에 관한 인자를 도출하고, 이를 기반으로 고성능, 장기간의 수명을 가지는 태양전지를 설계하고자 하였다.

1부에서는 \( sp^2 \) 탄소와 유기 태양전지에 대한 전반적인 소개를 하고, 이론적 고찰과 기존 연구 분석을 진행하여 태양전지의 성능과 수명에 대한 인자를 도출하였으며, 이를 기반으로 이번 연구에서 목표로 하는 고효율과 유연성을 만족시킬 수 있는 구조를 제안하였다.

2부에서는 1차원적인 구조를 가지는 공액 고분자를 기반으로 하여 고효율의 유기 태양전지를 구현하고자 하였다. 본 연구에서는 전기방사법을 이용하여 공액 고분자 나노 섬유를 성공적으로 준비하였고, 특히 대기의
습도에 민감한 기존 전기방사법의 문제점을 극복하고 습도와 관계없이 일정한 형태와 지름을 가지는 나노 섬유를 방사하는데 성공하였다. 전기방사법을 이용한 공액 고분자 나노 섬유는 기존 방법과는 다르게 고분자의 종류에 제한 받지 않고 나노 섬유로 방사가 가능하여 새롭게 합성된 고분자 중 하나인 PCDTBT 또한 나노 섬유 형태로 방사가 가능하였다. 전기방사된 PCDTBT 나노 섬유의 지름은 약 두 배에 해당하는 20 nm 정도였으며, 이를 기반으로 한 태양전지의 단락 전류 값은 11.54 mA/cm²이고 광전환 성능은 5.82 %로 기존 태양전지 대비 향상된 값을 보였다. 본 연구에서 제시된 제조방법은 일반적인 대기 환경에서 고성능의 태양전지를 구현할 수 있고, 새롭게 합성되고 있는 공액 고분자에 적용이 가능하여 높은 성능을 가지는 대면적 태양전지의 제조에 대한 가능성을 보였다.

3부에서는 환원된 산화 그래핀을 이용하여 유기 태양전지의 수명을 향상시키는 기체 차단성 필름의 제조와 성능에 대하여 연구하였다. 본 연구에서 준비된 산화 그래핀 용액을 유기 태양전지 기판 위에 간단하게 코팅하는 것만으로도 태양전지의 수명이 크게 향상됨을 알 수 있었으며, 기체 차단성에 의한 성능증가는 산화 그래핀의 분산성에 의해 크게 좌우된다는 것을 보였다. 또한 환원 조건의 제어를 통해 기체 차단특성을 더 향상시킬 수 있었는데, 그래핀의 표면을 평판하게 유지하고 필름의 표면적을 최소화함에 따라서 높은 기체 차단특성을 보임을 알 수 있었다. 마지막으로 환원된 산화 그래핀 기반 필름을 기체 차단성 필름으로, 단일벽 탄소나노튜브를 투명전도성 필름으로 하여 탄소 재료를 이용한 유연성
태양전지의 높은 수명을 구현하였다. 차후 연구에서 산화 그래핀 필름의 제조와 환원 방법을 개선함으로써 더 높은 유연성 태양전지의 성능을 얻을 수 있을 것으로 예측된다.

주요어: 태양전지, 탄소나노재료, 전기방사, 공액고분자, 나노섬유, 유연성디바이스
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