Nanoscale Mapping of Charge Transport Properties of Conjugated Polymer Films by Conducting Atomic Force Microscopy

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Conjugated Polymer: Excellent Organic Semiconductor

Semiconducting properties are due to the conjugation of \(\pi\)-electrons along the polymer chains and the delocalization of \(\pi\)-electrons between \(\pi\)–\(\pi\) stacking polymer chains.

http://www.chm.bris.ac.uk/webprojects2002/howell/LEPS/chemistry.html#
Charge-Carrier Transport

*p-type polymer*

\[
\begin{align*}
C_{6}H_{12}O & \rightarrow C_{6}H_{17}OC_{6}H_{17} \\
C_{8}H_{17}O & \rightarrow C_{6}H_{17}OC_{6}H_{17} \\
& \vdots \\
\end{align*}
\]

Amorphous silicon

\[
\begin{align*}
C_{6}H_{13} & \rightarrow C_{6}H_{13}C_{6}H_{13} \\
& \vdots \\
\end{align*}
\]

Hole Mobility

\[10^{-4} \quad 10^{-3} \quad 10^{-2} \quad 10^{-1}\]

\[\text{cm}^{2} \text{V}^{-1} \text{s}^{-1}\]

Electron Mobility

\[
\begin{align*}
C_{12}H_{25} & \rightarrow C_{12}H_{25}C_{12}H_{25} \\
& \vdots \\
\end{align*}
\]

*n-type polymer*
Light-Harvesting
Emission

http://www.shef.ac.uk/polopoly_fs/1.88176!/image/Molecular-materials-1.jpg
Good solubility in organic solvents and ease of preparation of uniform thin-films of polymer materials are suitable for the low-cost and large-scale device production based on the printing technology.
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Solar cell

By using these attracting properties of conjugated polymers...
Device Configuration based on Conjugated Polymers

Devices based on the conjugated polymers are usually consist of a thin film of a polymer or polymer blends sandwiched between electrodes with different WF.

Charge transport is universal and important process for the functionalization in all materials for electronic applications.
Charge Transport through a Hierarchical Nanostructure

- Chain ordering, packing
- Domain interface
- Phase separation

Function

Local charge transport

~ 100 nm

10 nm

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CAFM is a powerful tool for a nanoscale observation of charge transport. Electrical properties, such as conductivity, $I$–$V$ characteristics below the AFM tip can be measured at nanometer resolution.
Conductive Atomic Force Microscopy (C-AFM)

Spatial resolution \( \leq 20 \text{ nm} \)

Detection current \( \sim 0.3 \text{ pA} \)

C-AFM can provide the insight into both local charge transport properties and their spatial distribution in the film.
Our Approach

Polymer Solar Cell

Visualize nanostructures for charge carrier transport in the polymer films, which could determine the overall electronic functions of the materials.
1. Nanostructures for **hole transport** of \( p \)-type semicrystalline conjugated polymer films.


2. Nanostructures for **electron transport** of \( n \)-type conjugated polymer films.


3. Visualization of local charge transport of \( p/n \) conjugated polymer blend films for solar cell application.

Morphology-Dependent Hole Transport of P3HT Films

Poly(3-hexylthiophene) (P3HT)

One of the most widely used $p$-type conjugated polymers for electronic application.

Macroscopic charge transport

- Crystalline phase
- Amorphous phase

Thermal annealing

Voltage / V

Current density / mA cm$^{-2}$
Film Morphology Shows Little about Charge Transport

AFM surface topography

Macroscopic charge transport

Height / nm

Voltage / V

Current density / mA cm

X-ray scattering

Thermal annealing

P3HT film

Electrode
C-AFM Measurements

Spin-coating

P3HT film

55 nm

Au-coated AFM tip

Current

PEDOT:PSS

ITO

Hotplate

Piezo

Measurements:
- Spin-coating P3HT film
- Measure
- Annealing at 100°C
- Measure
- Annealing at 140°C
- Measure
- Annealing at 180°C
- Measure
Hole Current Images

As-spun

100 °C

140 °C

180 °C

Height / nm

0  6

As-spun

100 °C

140 °C

180 °C

Current / pA

30  135

poor conductive regions

~ 200 nm

good conductive regions
The relatively high current (high conductive) region in a film was outlined in black and relatively low current (low conductive) region was outlined in white, respectively.

Spatial distributions of the relatively high and low conductive regions in the annealed film are well correlated with those in the as-spun film.
Distribution of Good Conductive Regions

As-spun

180 °C-annealed

Annealing temperature / °C

Current / pA

Distance / nm

~ 200 nm

relatively high conductive regions

relatively low conductive regions

as-spun 100 140 180

Annealing temperature / °C

Current / pA
Growth of P3HT Nanocrystallites Measured by GIWAXS

As-spun

180 °C-annealed

predominantly face-on

\[ q_z / \text{Å}^{-1} \]

\[ q_y / \text{Å}^{-1} \]

\[ L_{100} / \text{nm} \]

\[ L_{010} / \text{nm} \]

Annealing temperature / °C

100 140 180

4.5 nm 12 nm 23 nm
Nanostructure for Efficient Hole Transport of P3HT

From C-AFM current image:
- Size of the high conductive region was ~200 nm.
- The locations of the relatively high conductive regions in the annealed film were well correlated with those in the as-spun film.

From GIWAXS analysis:
- The size of P3HT crystallites was only 10 ~ 20 nm.
- They grew in size by several nm after thermal annealing.

The relatively high conductive regions are assigned to the high density regions of P3HT nanocrystallites dispersed in the film.
For the high density regions, the electrical connectivity among the crystallites was effectively improved by the growth of individual crystallite size, leading to the formation of preferred hole-transporting pathways in the direction of film thickness.
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Design of Hole and Electron Injection Electrodes

PEDOT:PSS-coated ITO electrode

PEDOT:PSS

P3HT (p-type)

PEIE

PEIE

N2200 (n-type)

Selective Measurements of Hole and Electron Current

Energy level diagram

C-AFM local $I-V$

PEDOT:PSS electrode

HOMO

P3HT

Au

PEDOT:PSS electrode

HOMO

P3HT

Au

PEIE electrode

LUMO

P3HT

Au

PEIE electrode

LUMO

P3HT

Au

N2200 neat film

P3HT neat film

N2200 neat film

P3HT neat film

Current / pA

Voltage / V

Current / pA

Voltage / V
Nanostructures for Electron Transport of N2200

Topography

Electron current

Long-range ordering structures on \( \mu m \) length scale, which could not distinguished in the topographical image.
Nanostructures for Electron Transport of N2200

There is not a strong correlation between the topographical structures and the current magnitudes.

Electron-current image is considered to represent a difference in the density of locally ordered (fibril-like) polymer structures in the film.
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Direct observation of charge transport on a nanometer scale is critical for understanding a morphology-function relationship for the development of an efficient solar cell.
Local Charge Transport Properties of P3HT/N2200 Blend

- **P3HT/N2200 PEDOT:PSS**
  - 500 nm
  - Height / nm
  - 0-26

- **P3HT/N2200 PEIE**
  - 500 nm
  - Height / nm
  - 0-35

**local I–V**

Current / pA

Voltage / V

-2 -1 0 2

-15 -10 -5 0 5 10 15
Hole and Electron Transport in P3HT/N2200 Blend

The distribution of the hole- and electron-transport ability in the blend film were visualized by scanning the probe over the film surface.
Hole and Electron Transport in P3HT/N2200 Blend

- Hole current / pA
- Electron current / pA

Position / µm

Height / nm
Another advantage of the current imaging is its ability to reveal fine details of nanoscale structure of the blends, which is obscured in topographical imaging.
C-AFM current images reveal fine details of nanostructures for both hole- and electron-transport of polymer films, which are not easily distinguished in the topographical image.

The advantages of C-AFM to electrically resolve nanostructures of polymer films will contribute to further understanding of the mechanisms for the excellent charge transport and the creation of novel device functions.