

論文の内容の要旨

論文題目 Study on Nanostructure Control in Organic Electronic Devices

和訳 有機電子デバイスのナノ構造制御に関する研究

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1. Introduction

Electronic and optoelectronic devices using organic materials such as organic photovoltaic devices (OPVs), organic thin-film transistors (OTFTs), and organic light-emitting diodes (OLEDs) have been drawing tremendous attention from the viewpoints of both practical application as lightweight, flexible and low-cost electronic devices and fundamental scientific research to understand the electronic properties of the organic materials. To achieve a high performance in these devices, the formation of suitable nanostructures in both horizontal and vertical dimensions is of high importance since they largely influence the optical, mechanical and electrical properties of the organic films. Such nanofabrication methods could be generally categorized into two classes: top-down and bottom-up. Conventional top-down methods such as photolithography and patterned vacuum deposition techniques are now used for the fabrication of the structures for microelectronics. Alternative bottom-up approaches like nanoparticle formation, molecular self-organization and surface modification by self-assembly are relatively new and could provide with completely new prospective for the simple and low-cost fabrication techniques. In this thesis, the control of the nanostructure in the organic semiconductors in both horizontal and vertical dimensions are studied by using bottom-up approaches and investigate their application in OPVs and OTFTs.

In the first section, TiO₂ nanorod array was synthesized by a bottom-up approach and used as a pre-built nanostructure for the application to OPVs. In the second section, self-organization of molecular materials was utilized to control the vertical nanostructure in OPVs. In the third section, the detailed analysis was conducted to show that this novel surface structure formed by the self-organization during the wet coating process has a well-ordered monolayer structure. In the forth and fifth sections, this type of molecular self-organization at the solvent/air interface was applied for the high performance OTFTs. Finally, I will give the summary of this work.

2. Design and synthesis array of TiO₂ nanorods and its application in OPVs

Initial studies focused on the construction of inorganic nanostructures in the active layer of organic photovoltaic devices by using TiO₂ as the electron acceptor material and poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) as the electron donor polymer. For this purpose, a new method to fabricate an array of TiO₂ nanorod assemblies on a flat TiO₂ surface was developed. The TiO₂ nanostructures with a height of

approximately 40 nm were synthesized via a low temperature sol-gel reaction in a reversed micelle system (Figure 1). Devices with this interdigitating structure of MEH-PPV and single crystal TiO₂ nanorod assemblies show threefold improvement of short circuit current compared with the devices with the bilayer structure of MEH-PPV and flat TiO₂ (Figure 2). This improvement is attributed to the efficient exciton collection of the TiO₂ nanorod assemblies in the photovoltaic devices. Furthermore, the devices with the TiO₂ nanostructures show a comparable fill factor with that of the flat ones, which could be explained by the effective electron transport within the TiO₂ nanorods because of their single crystalline nature. These results demonstrate that the interdigitating structure with pre-built nanorod array has advantages in the exciton collection and charge transport, leading to the high fill factor and improved short circuit current. On the other hand, the interface area between donor/acceptor in this interdigitating structure was hardly comparable with mixture-type bulk heterojunction devices, which limited the overall device performance.

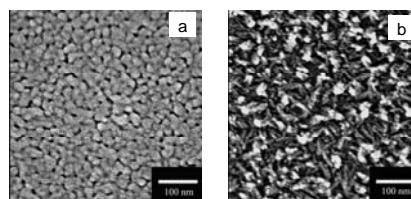


Figure 1 FESEM images of a) the flat TiO₂ substrate; b) the nanostructured TiO₂ substrate

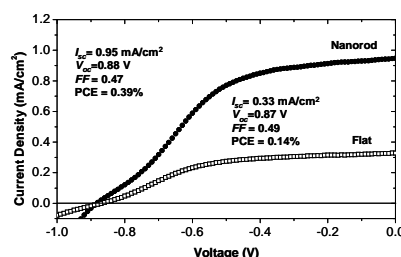


Figure 2. Current density-voltage curve of the MEH-PPV/TiO₂ photovoltaic devices under 100 mW/cm² AM 1.5 irradiation.

3. Layered nanostructure control by using self-organization

The ordered arrangement of materials at nanoscale is important not only in horizontal dimensions as shown in the previous section, but also in vertical dimensions since the vertical distribution of materials influences the intralayer and the interlayer carrier transports. For organic devices, it is often necessary to make multilayered structures to control the flow of the charge carriers inside the film and to match the energy level of the materials. Although the construction of such multilayer could be conducted by dry processes such as vacuum deposition, the solution-based processes are more attractive since they are scalable, low-cost and compatible with the various mass printing and coating techniques currently used in industry. However, there is an intrinsic difficulty for the solution-based multilayer formations because each layer has to be coated from an orthogonal solvent (i.e. the solvents used for the next layer cannot dissolve the previous layer). To solve this problem, a novel and simple approach to form layered nanostructures through molecular self-organization was developed in this work.

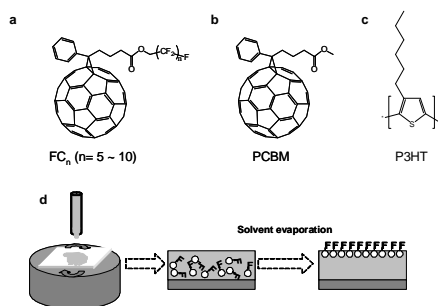


Figure 3 a) Chemical structure of FC_n , where n represents the number of fluorocarbons; b) chemical structure of PCBM; c) chemical structure of P3HT; d) schematic representation of the surface-segregated monolayer formation.

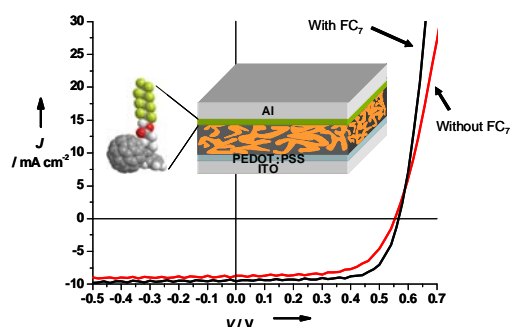


Figure 4 I - V characteristics under 100 mW/cm^2 AM1.5 illumination of P3HT: PCBM bulk heterojunction devices with FC_7 and without FC_7 .

It is well known that materials having a low surface energy such as fluorinated or silicone compounds prefer to migrate to the air/liquid interface during coating. Based on the idea to utilize this phenomenon, a novel fullerene derivative with a fluorocarbon chain (FC_7) was designed and synthesized. The C_{60} part works as an electron-accepting and transporting material and the perfluoroalkyl group gives a low surface energy to the material. When a small amount of FC_7 is mixed in the solution for spin coating, the FC_7 spontaneously migrates to the surface of the organic layer during spin casting due to the low surface energy of the fluorocarbon and forms a very thin layer of FC_7 in a single step (Figure 3). After the deposition of the metal electrode, it could act as a buffer layer between the polymer and the metal electrode, which may decrease the energy barrier for electron injection and collection because of the formation of the interfacial dipole layer. As the result, the fill factor of the OPV devices significantly increased to a value of more than 70%, which directly contributed to the improvement of the power conversion efficiency up to 3.79% (Figure 4).

4. Molecular structure of surface-segregated FC_7 thin layer

As shown in the previous section, the OPVs with the surface-segregated FC_7 thin layer show improved device performance, particularly the fill factor and short-circuit current. To clarify the functions of FC_7 thin layer, the molecular structure of the surface-segregated FC_7 thin layer was further studied by sum-frequency generation (SFG) spectra in the collaboration with Prof. Shen Ye at Hokkaido University. Strong SFG signal from FC_7 /air interface suggest FC_7 molecules have an ordered and oriented structure on the surface of organic layer (Figure 5a). Surprisingly, along with changing the length of the fluorinated chain, the intensity of SFG signal clearly shows odd-even effect (Figure 5c and 5d). It reveals that the FC_n molecules should have very good packing on the surface of organic layer despite the easiness of the preparation. I named

this new class of well-ordered monolayer “surface-segregated monolayers” (SSMs), which gives a promising approach to modified the surface of organic semiconductors, and therefore can be applicable to various organic devices.

5. Organic thin film transistors based on surface-segregated thin layer

As in the discussion of the previous section, the surface segregation of the low surface energy materials was driven by minimization of the total energy. Besides fluorocarbon chains, alkyl chains also show relatively low surface energy. It was reported that spin coated films of poly(3-hexylthiophene) (P3HT) oriented with the side chains normal to the substrate at the solution-to-air interface. This orientation could be attributed to the low surface energy of alkyl side chains that prefer to migrate to the air/liquid interface to minimize the total energy of the system. Interestingly, this molecular orientation was favorable for field-effect mobility in thiophene-containing polymers. If the transistors can be constructed in this oriented layer and study the carrier transport, it could provide new information of the electronic properties of these

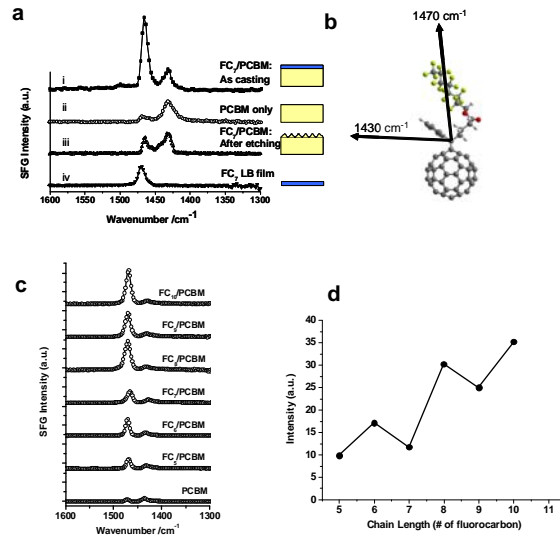


Figure 5 a) SFG spectra (*ssp*) of FC₇/PCBM, PCBM, and FC₇/PCBM films after plasma etching and of FC₇ LB film; b) The calculated optimized structure of FC₇ by DFT. The arrows represent the dipole derivative vectors of the vibration modes at 1470 cm⁻¹ and 1430 cm⁻¹, respectively; c) SFG spectra (*ssp*) of PCBM, FC₃/PCBM, FC₆/PCBM, FC₇/PCBM, FC₈/PCBM, FC₉/PCBM and FC₁₀/PCBM films; (b) plot of the SFG signal intensities vs. the number of fluorocarbons.

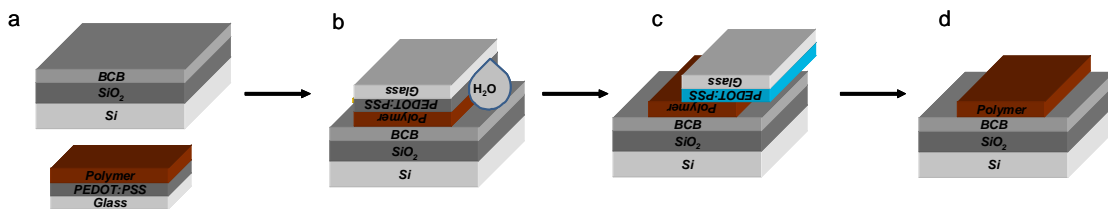


Figure 6. A schematic images depict the transfer process applied to the deposition of a Polymer film onto dielectric layer; a) Prepared two substrates with different structures: /BCB/SiO₂/Si and Glass/PEDOT:PSS/Polymer film for transfer stamp; b) lightly laminated two substrates together and put a drop of water on the edge; c) Polymer film was detached with glass substrate after the PEDOT:PSS layer was dissolved; d) remove the glass substrate, leaving the desired polymer film on target substrates.

materials.

To investigate the carrier transport in surface-segregated thin layer, a novel film transfer approach based on contacting and floating off process of the organic films was developed in this work (Figure 6). Organic films can be transferred onto other organic film surfaces with the sizes more than several square centimeters without apparent damage by this method. Transistors are fabricated based on three batches of P3HT and other seven types of thiophene-based polymers (Figure 7a). Very interestingly, all the transistors prepared by the contact film transfer achieve mobility higher than $0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and these values are one to two orders magnitude higher than those of the transistors prepared by the conventional spin coating method (Figure 7b). This improvement could be attributed to the better chain orientation and interchain π -interaction at the air/solvent interface induced by the low surface energy and molecular self-organization during the spin-coating process.

6. Multilayered ambipolar transistors and inverters fabricated by contact film transfer

In the previous section, a novel film transfer was developed to study the carrier transport in surface-segregated thin layers. The benefits of this approach can be also demonstrated by the fabrication of the ambipolar OTFTs based on a bilayer structure of P3HT/PCBM. Furthermore, the interfacial properties between these films can be controlled by the combination with SSMs.

The schematic image of the prepared bilayer transistor is shown in inset of Figure 8a. The output characteristics are shown in Figure 8a. Clear field effect was observed in both p - and n -channel operation. The output curve shows diode-like behavior at low gate voltage (V_G) and high drain-to-source voltage (V_{DS}). This is a typical character in ambipolar transistors and observes in neither P3HT nor PCBM unipolar transistors. From the slope of $I_D^{1/2}$ versus V_G at V_D

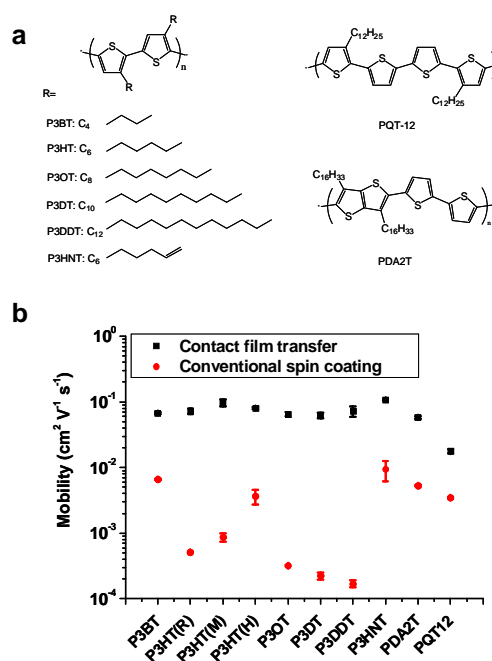


Figure 7. a) Chemical structures of thiophene-containing polymers discussed in this work; b) Plot of field-effect mobility versus different polymers. Transistors fabricated by contact film transfer are represented by black circles, and transistors fabricated by spin coating are represented by red circles.

= +30 V and -30 V, the electron mobility of $2.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the hole mobility of $1.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the ambipolar devices can be extracted. The ambipolar mobilities achieved in this work are the highest values among the two-component transistors based on solution-processes reported to date. Although it still lower than the record value from single-component ambipolar FETs, this approach can be easily applicable to the other organic materials with higher mobilities. In addition, the bilayer ambipolar transistors showed balanced electron and hole mobility of high degrees, therefore it could be a potential candidate for the application in organic complementary inverters. Inverters were fabricated by connect two identical ambipolar P3HT/PCBM

transistors on a single substrate (Figure 8b). With $V_{DD} = 75 \text{ V}$ and -75 V , a high output voltage gain of 14 is achieved which is defined as the steepness of the characteristics at the transitions between high and low states (Figure 8c). The output voltage swing could be controlled by changing supply voltage V_{DD} from -75 V to $+75 \text{ V}$. This result demonstrates the usefulness of the contact film transfer approach to fabricate various electronic devices in very simple steps.

7. Summary

In this work, nanostructure control in organic devices by using bottom-up approaches is studied. Novel concepts are proposed to improve the device performance in OPVs and OTFTs through nanostructure control. These concepts and approaches are general and applicable to other types of organic semiconductors and to the various other organic devices.

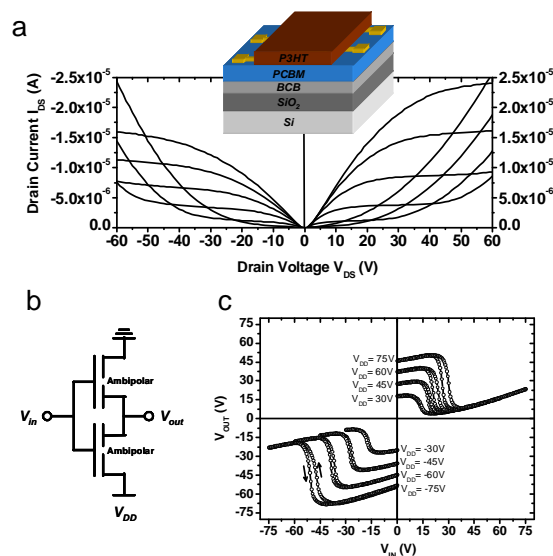


Figure 8. a) The output characteristics of the P3HT/PCBM bilayer transistor. The gate voltages ranges from 0 to -60 V (-10 V increments) for holes and from 0 to 60 V (+10 V increments) for electrons; b) A schematic representation of the electrical connections in the inverter; c) Transfer characteristics of CMOS-like inverters based on two identical ambipolar transistors.