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研究課題名（和文）Bottom-up Construction of Semi-Conductive/Ferroelectric Polymer Hybrid Nanofilms for Flexible Devices

研究課題名（英文）Bottom-up Construction of Semi-Conductive/Ferroelectric Polymer Hybrid Nanofilms for Flexible Devices

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研究成果の概要（和文）：本研究では、ラングミュアーブロジェット（LB）法を利用して分子レベルで強誘電性高分子ポリフッ化ビニリデン（PVDF）の機能性単分子膜の作製に成功した。特に、PVDF／半導体高分子のハイブリッドナノシートを様々な混合比で数ナノスケール精度で構築した。PVDF相の結晶相はほぼ100%の強誘電相であることを示した。PVDF相に由来する残留分極を利用して半導体相の電荷移動を制御し、抵抗スイッチングに基づく有機不揮発性メモリを実現した。一方、PVDFナノシートは、有機トンネル障壁層としてスピンバルブデバイスにも適用された。室温付近（300K）で磁気抵抗比が2.5%を超える結果を世界で初めて報告した。

研究成果の概要（英文）：Bottom-up preparation of ferroelectric poly(vinylidene fluoride) (PVDF) was succeeded at nanometer-precision for developing memory devices including resistive nonvolatile memories and spin-valves, etc. First, ferroelectric PVDF/semiconductive polythiophene hybrid monolayers were successfully fabricated at varying blend ratios from the Langmuir-Blodgett method. The PVDF matrix in the hybrid nanosheets contains almost 100% ferroelectric phase. Ferroelectric non-volatile memories were realized owing to the ferroelectricity-manipulated resistive switching. On the other hand, the PVDF LB nanosheets were applied as insulator tunnel layer in spin valves of Co/PVDF/Fe304. It is noteworthy that the magnetoresistance (MR) effect was even observed at 300 K with a MR ratio exceeding 2.5%, which is achieved for the first time in such organic devices. Therefore, the ferroelectric PVDF hybrid nanosheets are promising candidates for various organic electronics with outstanding performance.

研究分野：高分子・繊維材料

キーワード：Bottom-up method　Ferroelectric polymer　Semi-conductive polymer　Non-volatile memories　Spin valves　Langmuir-Blodgett　Polymer blends

１．研究開始当初の背景

Recently, tremendous efforts have been dedicated toward organic resistive switches based on phase-separated ferroelectric–semiconductor blends on account of the tunable injection barrier. The reversible built-in field caused by ferroelectric polarization will provide a new strategy to precisely adjust charge transfer and accumulation properties of the electronic devices, thereby leading to generation of novel functionalities or enhanced performance (K. Asadi, et al, Nat. Mater., **7,** 547 (2008); K. Asadi, et al, Adv. Funct. Mater. **19**, 3173, (2009).)

It has been determined that the nanoscale morphology of a phase-separated blend of the two polymers is critical in device performance, requiring a strong ferroelectric matrix and optimized semi-conductive crystal domains with sizes smaller than 50 nm. However, traditional methods such as spin coating method cannot achieve fine control of nanoscale separation structures and film thickness.

I have successfully utilized a bottom-up Langmuir-Blodgett method to prepare ferroelectric poly(vinylidene fluoride) (PVDF) nanosheets (Macromolecules, **45**, 9076, (2012); Soft Matter, **11**, 1962 (2015)). Surprisingly, outstanding results were achieved over the traditional top-down methods (e. g. spin-coating): 1). smooth surface morphologies and regular layer structures (2.3 nm per layer) without substrate selectivity; 2). spontaneous and ultrahigh ferroelectric β crystal content (approximately 100 %) with no complicated post-treatments; and 3) enhanced ferroelectricity with the highest ferroelectric polarization for nano-scale films without any electrical poling and long endurance owing to the high orientation of β crystals (J. Mater. Chem. C, **2**, 6727, (2014)). To extend their applications, the PVDF LB nanofilms were developed and applied as a platform and matrix to combine with other functional materials, like organic functional materials or inorganic nanoparticles for various organic electronics during the period of this project.

２．研究の目的

First, developing a bottom-up construction of ferroelectric polymer/functional semi-conductive polymers hybrid nanofilms (nano-building-blocks) was carried out through in situ mixing at the air-water interface or by alternatively deposition of semi-conductive polymer monolayers and the aforementioned PVDF monolayers.

Second, through optimizing the synergistic effect of spreading solvent and air-water interface, the simultaneous formation of PVDF nano-scale matrix owning the complete ferroelectric phase, and the ultrafine semi-conductive polymer domains e.g. regio-regular poly(3-carboxy-pentyl-thiophene) (P3CPenT) with regular crystal structures were pursued. From another viewpoint, the preparation method afforded much information to modulating the nanostructures of polymer nano-blends because of the molecular-level adjustment.

Then, the polymer hybrid nano-building-blocks are promisingly applied in flexible electronics including resistive switching nonvolatile memories (RSNMs). Through film thickness control, the ferroelectricity manipulation of charge charrier and recombination in such devices were systematized and optimized, thereby leading to a theoretical system for the application of polymer LB films in various devices possessing ferroelectricity-modulated properties.

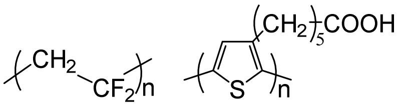
３．研究の方法

First, the optimum fabrication condition was found at different sub-phase temperature and mixing ratio of PVDF to P3CPenT by Langmuir-Blodgett technique. Then, characterization of film properties was conducted using XRD, SEM, AFM, etc. Electronic devices were fabricated using a simple sandwich construction of electrode/PVDF hybrid nanosheets/electrode. The device performance was investigated in details using Kelvin force microscopy (KFM), Sawyer-Tower method and so on. Spin valves and energy generators were also exploited for new applications of such PVDF hybrid LB nanofilms.

４．研究成果

(1) Preparation and characterization of PVDF/P3CPenT hybrid nanosheets using Langmuir-Blodgett method

Ferroelectric PVDF/semiconductive polythiophene (P3CPenT) hybrid monolayer building-blocks were developed at varying blend ratios using LB technique at 20 ^{o}C (**Scheme 1 and Fig. 1**). The multilayered hybrid nanosheets show much improved surface roughness even at 9:1 ratio of PVDF to P3CPenT which is more applicable for electronics applications than spin-cast films. Because of the precisely controllable bottom-up construction, semiconductive polymer domains were modulated from nanoparticles to nanofiber structures by increasing the content of P3CPenT into the ferroelectric matrix. Moreover, the ferroelectric matrix contains almost 100% β crystals: a polar crystal phase responsible for ferroelectricity of PVDF. [*RSC Advances*, 2018, **8**, 7963-7968.]



PVDF **P3CPenT**

Scheme 1 Chemical structures of PVDF and P3CPenT.

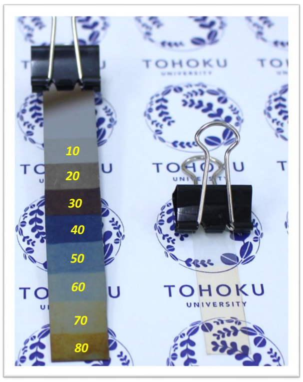


Fig.1 PVDF/P3CPenT hybrid LB nanofilms on silicon and PET substrates.

(2) Development of organic ferroelectric non-volatile memories and their performance

Ferroelectric nonvolatile memories based on the hybrid nanosheets were demonstrated with resistive switching properties along with the reversal of ferroelectric polarization direction (**Fig. 2**). The ON/OFF ratio values and retention time are superior to most of the previously reported values, indicative of a great potential for application of such hybrid nanosheets to flexible electronics. The devices show reversible switching over many cycles up to 1000 cycles in spite of a little linear decrease of ON-current and increase of OFF-current as a function of cycle numbers, which is consistent with the reported values. The retention of current density was demonstrated with consistent current density at the ON state up to 4 days and the OFF state up to 30 days. A slight degradation of current density at the ON state was observed after 4 days, which might be ascribed to the interfacial charge induced depolarization of ferroelectric domains.
[*RSC Advances*, 2018, **8**, 7963-7968.]

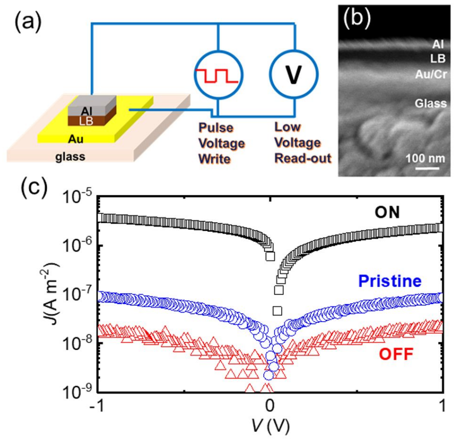


Fig. 2 (a) Schematic illustration of a ferroelectric non-volatile memory and its operation process, (b) the cross-sectional SEM image of the device and (c) the read-out current at opposite polarization direction of the ferroelectric PVDF.

(3) Development of organic spin-valves and their performance

Ferroelectric poly(vinylidene fluoride) (PVDF) nanofilms have been fabricated by the Langmuir–Blodgett technique, possessing mainly ferroelectric active phase and controllable film thickness by 2.3 nm per layer. Atomic force microscopy technique and Fourier transform infrared spectroscopy were utilized to characterize the film properties. Importantly, the PVDF films could act as the barrier layer to prepare spin transport devices using Fe_3O_4 and Co as the bottom and top ferromagnetic electrodes, respectively (**Fig. 3a**). Spin-dependent electron transport behaviors were systemically studied in these devices by varying PVDF film thickness from 3 layers (7 nm) to 13 layers (30 nm). With increasing PVDF layer numbers, magnetoresistance (MR) response decreases likely subjecting to the change of spin transport from the tunneling to hopping transport. The investigated MR effect was dependent on operation temperatures (150 K, 200 K, 250 K and 300 K). It is noteworthy that the MR effect was even observed at 300 K with a MR ratio exceeding 2.5%, which is achieved for the first time in such organic devices (**Fig. 3b**). The device performance could be further improved at the lower operation temperatures. MR ratios, device resistances and electron transport mechanisms in the present devices were also discussed to analyze the spin transport behaviors. The results indicate that the ferroelectric PVDF nanofilms are promising candidates for spin devices operated at room temperature, thereby shedding light on the design of organic ferroelectric spintronics with a higher performance.

[*Journal of Materials Chemistry C*, 2017, **5**, 5055-5062.]

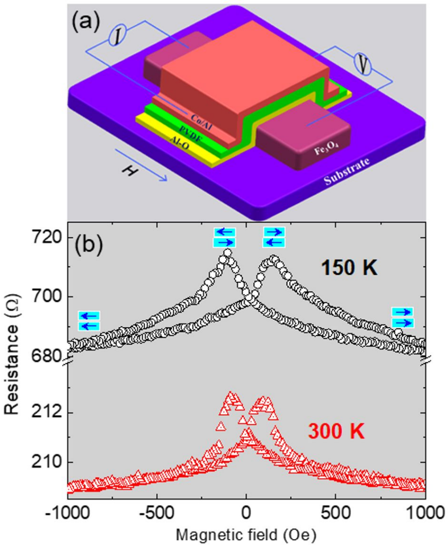


Fig. 3 (a). Schematic illustration of the ferroelectric spin valve with a sandwich device structure of Fe_3O_4/PVDF LB/Co and (b) Magnetoresistance curves for spin valve device with 3-layer PVDF measured at 300 K (red line) and 150 K (black line).

(4) Development of flexible energy generators based on PVDF/P3CPenT hybrid LB nanosheets

Flexible energy generators were fabricated based on PVDF/P3CPenT hybrid LB nanosheets which was deposited onto ITO/PET substrates (**Figs. 1a and b**). The top electrode was conductive PEDOT-PSS. The device showed smart response to the external finger press which generated different voltage signal at millivolt scale for slight press and heavy press (**Fig. 4c**).

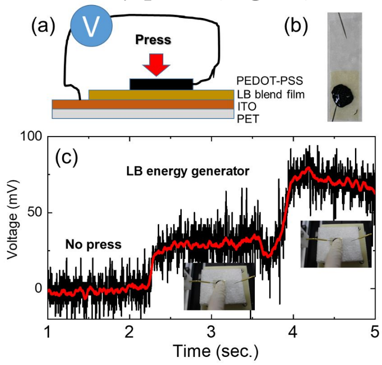


Fig. 4 (a) Flexible energy generator based on PVDF/P3CPenT hybrid LB, (b) the real device and (c) voltage curve vs finger press.

５．主な発表論文等

〔雑誌論文〕（計 4 件）

(1) **Huie Zhu***, Shunsuke Yamamoto, Jun Matsui, Tokuji Miyashita, Masaya Mitsuishi*, Resistive non-volatile memories fabricated with poly(vinylidene fluoride)/poly(thiophene) blend nanosheets.
RSC Advances, 2018, 8, 7963-7968, DOI:10.1039/C8RA01143E. **査読有**

(2) Xianmin Zhang*, Junwei Tong, **Huie Zhu***, Zhongchang Wang, Lianqun Zhou, Shouguo Wang, Tokuji Miyashita, Masaya Mitsuishi, Gaowu Qin, Room Temperature Magnetoresistance Effect in Ferroelectric Poly(vinylidene fluoride) Spin Valves.
Journal of Materials Chemistry C, 2017, 5, 5055-5062, DOI:10.1039/C7TC00517B. **査読有**

(3) **Huie Zhu***, Buket Akkus, Yu Gao, Yida Liu, Shunsuke Yamamoto, Jun Matsui, Tokuji Miyashita, Masaya Mitsuishi*, Regioselective Synthesis of Eight-Armed Cyclosiloxane Amphiphile for Functional 2D and 3D Assembly Motifs.
ACS Applied Materials & Interfaces, 2017, 9, 28144-28150, DOI: 10.1021/acsami.7b07331.
査読有

(4) M. Mahbubul Bashar, **Huie Zhu**, Shunsuke Yamamoto and Masaya Mitsuishi*, Superhydrophobic surfaces with fluorinated cellulose nanofiber assemblies for oil-water separation.
RSC Advances, 2017, 7, 37168-37174, DOI:10.1039/C7RA06316D. **査読有**

〔学会発表〕（計 19 件）

(1) **Huie Zhu**, Buket Akkus, Shunsuke Yamamoto, Jun Matsui, Tokuji Miyashita, Masaya Mitsuishi,
Room Temperature Mineralization of Cyclosiloxane Supramolecule Monolayers toward Ultrathin Silica Films
第65回応用物理学会春季学術講演会, (2018).

(2) **Huie Zhu**, Masaya Mitsuishi, High-Performance Interfacial Assemblies of Functional Polymers and Supramolecules,
The 7th International Symposium of Green MAP Center and LPIC (GMAP/LPIC 2018), (2018). 招待講演

(3) **Huie Zhu**, Tillman Jan Buchtal, Shunsuke Yamamoto, Tokuji Miyashita, Masaya Mitsuishi
Amphiphilic Cyclosiloxane Supramolecules toward Unique Self-Assembly Nanostructures
CEMS International Symposium on Supramolecular Chemistry & Functional

Materials 2018, (2018).
(4) Chang Fu, **Huie Zhu**, Shunsuke Yamamoto, Tsunenobu Onodera, Hidetoshi Oikawa, Masaya Mitsuishi,
Spontaneous formation of poly(vinylidene fluoride) nanoparticles with dominant electroactive phase,
CEMS International Symposium on Supramolecular Chemistry & Functional Materials 2018, (2018).
(5) Chang Fu, **Huie Zhu**, Shunsuke Yamamoto, Tsunenobu Onodera, Hidetoshi Oikawa, Masaya Mitsuishi,
Interfacial Preparation of Ferroelectric Polymer Nanoparticles,
Tohoku-Melbourne Symposium on Advanced Materials---Scientific & Engineering Challenges, Part4, (2017).
(6) **Huie Zhu**, Shunsuke Yamamoto, Masaya Mitsuishi,
A Mussel-Inspired Cyclosiloxane Supramolecule for Air-Stable Self-Assembly Coatings,
第66回高分子討論会, (2017).
(7) 付 暢, 朱 慧娥, 三ツ石 方也,
液－液相界面を介したポリフッ化ビニリデン（PVDF）ナノ粒子の作製,
第66回高分子討論会, (2017).
(8) 三ツ石 方也, でみるちあり, 朱 慧娥, 山本 俊介, 宮下 徳治
環状シロキサンによるソフトマテリアルデザイン
日本セラミックス協会第30回秋季シンポジウム, (2017). 招待講演
(9) 朱 慧娥, Akkus Buket, 山本　俊介, 宮下 徳治, 三ツ石 方也
Photoinduced Silica Nanostructures Based on Cyclosiloxane Supramolecule Assemblies at Room Temperature
2017年光化学討論会, (2017)
(10) 劉 一達, 朱慧娥, 山本 俊介, 渡辺 明, 宮下 徳治, 三ツ石 方也
Flexible Hybrid Nanoparticle Assemblies for High Sensitive SERS and UV detection
2017年光化学討論会, (2017)
(11) Im Yongjoon, 高 宇, 朱 慧娥, 山本 俊介, 松井 淳, 宮下 徳治, 三ツ石 方也
ピレン含有フッ素系両親媒性高分子ナノ粒子薄膜の発光特性
2017年光化学討論会, (2017).
(12) Hiroaki Ohara, Shunsuke Yamamoto, **Huie Zhu**, Hidetoshi Oikawa, and Masaya Mitsuishi
Layer-by-Layer Deposition and Crystal Growth Control of Metal Organic Frameworks Films on Polymer Thin Films
14th European Conference on Molecular Electronics, (2017).
(13) Hiroaki Ohara, Shunsuke Yamamoto, **Huie Zhu**, Hidetoshi Oikawa, Masaya Mitsuishi
Layer-by-Layer Deposition and Crystal Growth Control of Metal Organic Frameworks Nanoassembly on Polymer Films
Tohoku University's Chemistry Summer School 2017, (2017).
(14) Fu Chang, **Huie Zhu**, Masaya Mitsuishi
A Study on Poly(vinylidene fluoride) Nanostructure Formation at Inhomogeneous Interface
第45回東北地区高分子若手研究会夏季ゼミナール, (2017).
(15) Soyeon Kim, Yida Liu, Ali Demirci, **Huie Zhu**, Shunsuke Yamamoto, Masaya Mitsuishi
Synthesis of Cyclic Siloxane Polymers Containing Dynamic Covalent Functional Groups
第45回東北地区高分子若手研究会夏季ゼミナール, (2017)
(16) 大原 浩明, 山本 俊介, 朱 慧娥, 及川 英俊, 三ツ石方也
高分子薄膜上への金属有機構造体ナノ薄膜の積層と結晶成長制御
第66回高分子学会年次大会, (2017).
(17) 赤塚 亜紗美, 朱 慧娥, 山本 俊介, 三ツ石 方也, 宮下 徳治, 松井　淳
両親媒性かご型シルセスキオキサンを用いたハイブリッドナノプレートの構築
日本化学会第97春季年会, (2017).
(18) 大原 浩明, 山本 俊介, 朱 慧娥, 及川 英俊, 三ツ石方也
高分子薄膜上への金属有機構造体薄膜の成長制御
第64回応用物理学会春季学術講演会, (2017).
(19) 朱 慧娥
Cyclosiloxane Supra-Amphiphiles Building Blocks: Synthesis, Assemblies, and Applications
平成28年度東北地区先端高分子セミナー, (2017). 招待講演

〔図書〕（計 1 件）
(1) 三ツ石 方也, 高 宇, 朱 慧娥, 山本 俊介, 宮下 徳治, 高分子微粒子ハンドブック「第8章3 フッ素系両親媒性高分子を利用した微粒子薄膜の作製と機能」
シーエムシー出版, 2017, 230-236.

〔産業財産権〕（計 0 件）

〔その他〕
ホームページ等
http://www.tagen.tohoku.ac.jp/labo/mitsuishi/index.html

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