Academic Program [Oral A] | 20. Materials Chemistry -Basic and Application-：Oral A

Thu. Mar 27, 2025 9:00 AM - 11:30 AM JST | Thu. Mar 27, 2025 12:00 AM - 2:30 AM UTC
[G]3402(3402, Bldg. 3, Area 4 [4F])

[[G]3402-2am] 20. Materials Chemistry -Basic and Application-

Chair: Kensuke Naka, Takaaki Tsuruoka

English
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[[G]3402-2am-01]

Observation of neuromorphic behavior in Cu-based metal-organic framework

○Dildora Khakimboeva[1], Takashi Kitao[1,2], Ryo Nakayama[1], Taro Hitosugi[1], Takashi Uemura[1] (1. The University of Tokyo, 2. JST-PRESTO)

Japanese
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[[G]3402-2am-02]

Polymerization of cubane in a MOF toward synthesis of carbon nanothreads

○Ryo Takahashi[1], Takashi Kitao[1,2], Takashi Uemura[1] (1. Graduate School of Engineering, The University of Tokyo, 2. JST-PRESTO)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[[G]3402-2am-03]

Construction of Sn-based perovskite/Sn MOF composites

○Haruka Nishijima[1], Yohei Takashima[1], Kensuke Akamatsu[1], Takaaki Tsuruoka[1] (1. Konan Univ.)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[[G]3402-2am-04]

Development of functional materials utilizing properties exhibited in sub-nanoscale spaces

○Kosei Hayashi[1], Hiroto Watanabe[2], Hiroaki Imai[2] (1. Tokyo Metropolitan Industrial Technology Research Institute, 2. Keio University)

9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC

Break

English
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[[G]3402-2am-05]

Fabrication of Fluorinated Polymer Hybrid Materials with Highly Fluorinated POSS Fillers for Reducing the Refractive Index

○Tatsuaki Kunimitsu[1], Masayuki Gon[1], Kazuo Tanaka[1] (1. Grad. Sch. of Eng., Kyoto Univ.)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[[G]3402-2am-06]

Development of gas separation membranes utilizing intramolecular vacancies in caged silsesquioxanes

○Haruki Ogawa[1], Masayasu Igarashi[2], Kazuki Yamamoto[1], Takahiro Gunji[1] (1. Tokyo University of Science, 2. National Institute of Advanced Industrial Science and Technology)

🏷 Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[[G]3402-2am-07]

Synthesis of polysilsesquioxanes with hexyl groups as side chains and preparation of non-solvent induced phase separation membranes

○Yu Tomizawa[1], Kazuki Yamotomo[1], Gunji Takahiro[1] (1. Tokyo university of science)

🏷 Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[[G]3402-2am-08]

Synthesis of butene-butyne bridged alkoxysilanes and preparation of reverse osmosis membranes

○Kota Aizawa[1], Kazuki Yamamoto[1], Gunji Takahiro[1] (1. Tokyo University of Science)

10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC

Break

🏷 Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[[G]3402-2am-09]

Curing by polysilsesquioxane films on boron catalyst

○Haruto Sato[1], Kazuki Yamomoto[1], Takahiro Gunji[1] (1. Tokyo University of Science)

🏷 Japanese
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[[G]3402-2am-10]

Superhydrophobic coatings based on the surface-modified nanosheets

○Hisafumi Sudo[1], Yuta Nishina[2], Hiroaki Imai[1], Yuya Oaki[1] (1. Keio University, 2. Okayama University)

🏷 Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[[G]3402-2am-11]

Thermal properties of polystyrene loaded with boron nitride filler

○Koichi Honda[1] (1. Osaka University)

🏷 Japanese
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[[G]3402-2am-12]

Development of a surface treatment method using zinc oxide as a binder layer for thermoplastic elastomers with PBT as a hard segment

○Sachio Yoshihara[1], Yukika Otawa[1], Ikuko Nakazawa[1], Yoshifusa Ishikawa[2], Kenichiro Motoi[2], Tetsushi Oikawa[2] (1. Utsunomiya University, 2. Nippon Platec Co. Ltd.)

🏷 Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[[G]3402-2am-13]

Surface modification of biodegradable polymer/ hydroxyapatite complex (I) -Introduction of etidronic acid-

○Rin ITO[1], Masahiro FUJITA[1], Masahiro RIKUKAWA[1], Yuko TAKEOKA[1] (1. Faculty of Science and Engineering, Sophia Univ.)

Observation of neuromorphic behavior in Cu-based metal-organic framework

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Graduate School of Science, The University of Tokyo*) ○Dildora Khakimboeva,[1] Takashi Kitao,[1] Ryo Nakayama,[2] Taro Hitosugi,[2] Takashi Uemura[1]

Keywords: *Artificial synapse*; *Neuromorphic system*; *Proton conductivity*; *Metal-organic framework*

Neuromorphic systems have gained attention as a solution to the limitations of silicon-based computing, which faces challenges in scaling and slow memory access.[1] One of the key components of a neuromorphic system is the artificial synapse, which adapts to stimuli by adjusting synaptic plasticity. Among various emerging materials, metal-organic frameworks (MOFs) offer advantages such as tunable porosity and adaptable chemical properties, both of which are essential for modulating synaptic plasticity.[2] However, the neuromorphic behavior of MOFs remains elusive. Herein, a neuromorphic devise based on a MOF was fabricated to investigate conductance changes in response to pulse stimulation.

$Cu_3(BTC)_2$ (**1**; BTC = 1,3,5-benzentricarboxylate) thin films were synthesized using an in-situ growth method. The copper substrate was dipped into a DMF/ethanol solution containing H_3BTC, and then heated under air at 80 ºC for 6 hours, producing a uniform thin film. The formation of **1** was confirmed by XRD and SEM measurements. Alternating current impedance measurements were carried out under vacuum and water vapor, demonstrating the proton-conducting properties of MOF **1**. Two repetitive pulse voltages (1 V, 10 ms) were applied to evaluate changes in conductance under water vapor, which is crucial for constructing a neuromorphic system. Notably, a change in conductance responding to pulse stimuli was observed, and the second stimulus induced a larger change. These results suggest short-term plasticity of MOF **1** based on proton conductivity (Fig. 1).

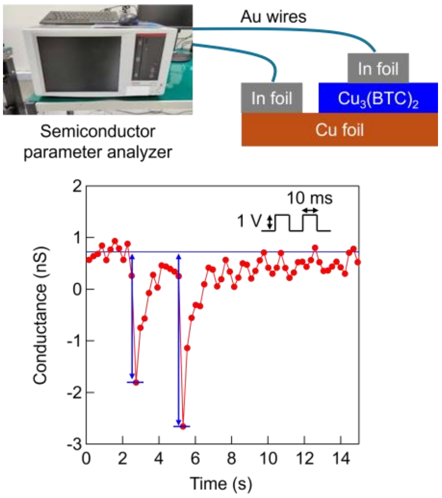

Fig. 1 (top) Device fabrication for pulse conductivity measurements. (bottom) Paired-pulse facilitation function emulated by 2 consecutive pulses under water vapor. Conductivity was measured by evaluating the current when applying a voltage of 0.01 V.

REFERENCES

1. Y. V. D. Burgt, *et al*., *Nat. Electron*., **2018**, *1*, 386.
2. S. V. Bachinin, *et al*., *Commun. Mater*., **2024**, *5*, 128.

カーボンナノスレッド創製に向けたMOF空間内キュバン重合

（東大院工 [1]・JST さきがけ [2]）○髙橋遼 [1]・北尾岳史 [1,2]・植村卓史 [1]

Polymerization of cubane in a MOF toward synthesis of carbon nanothreads

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*JST-PRESTO*) ○ Ryo Takahashi,[1] Takashi Kitao,[1,2] Takashi Uemura[1]

Carbon nanothreads (CNThs) are an emerging class of one-dimensional (1-D) sp^3 carbon nanomaterials that have recently attracted increasing attention due to their exceptional properties, such as high thermal conductivity and tensile strength. Although the production of CNThs was achieved by compressing molecular precursors at high pressure in diamond anvil cells, this method lacks scalability due to the limited available reaction areas.[1] Metal-organic frameworks (MOFs) can provide an ideal compartment for controlling the arrangement of guest species within the nanochannels. Here, we report controlled polymerization of cubane utilizing a MOF toward bulk-scale synthesis of a CNTh (Fig. 1). Molecular dynamics simulations show that cubane molecules are densely aligned along the nanochannels of the MOF. A series of characterization methods for the product, including MALDI-TOF MS, FT-IR, and NMR spectroscopy measurements, suggest the formation of the CNTh composed entirely of sp^3 bonds.

Keywords：Metal−organic frameworks, Carbon nanothreads

カーボンナノスレッド(CNTh)とは sp^3 結合のみから構成される一次元ナノ炭素材料である。ダイヤモンド構造に由来する優れた熱伝導性や機械特性、さらには柔軟性を併せ持つ物質として、近年大きな注目を集めている。しかし、従来の合成手法では数万気圧もの超高圧環境を要することに加えて、枝分かれ構造の存在やスケールアップに課題があった [1]。本研究では、わずか 0.2 nm の幅しかない最細 CNTh の創製を目指し、多孔性金属錯体(MOF)の一次元細孔を利用したキュバンの制御重合を行った(Fig. 1)。

大気圧下でキュバンを加熱すると、炭素-炭素結合が開裂し、即座にベンゼンなどの最安定構造へと変化する。一方、MOF の一次元細孔内で加熱を行うと、高密度に配列されたキュバン分子同士での結合形成が促進され、重合生成物を得ることに成功した。FT-IR、MALDI-TOF MS、NMR 測定から、得られた生成物は sp^3 結合のみから構成される CNTh であることが示唆された。

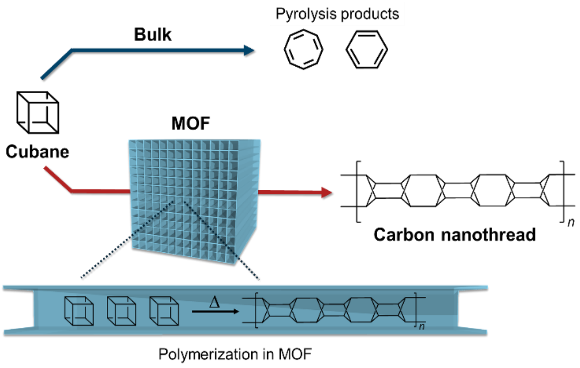

Fig. 1 Schematic image for preparation of a thinnest CNTh in the bulk scale using an MOF as template.

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1) H. T. Huang, *et al.*, *J. Am. Chem. Soc.*, **2020**, *142*, 17944–17955

Sn ベースペロブスカイト半導体/Sn MOF 複合体の作製

(甲南大学)○西島 遥・髙嶋 洋平・赤松 謙祐・鶴岡 孝章

Construction of Sn-based perovskite/Sn MOF composites

(Department of Nanobiochemistry, Frontiers of Innovative Research in Science and Technology, Konan University) ○Haruka Nishijima, Yohei Takashima, Kensuke Akamatsu, Takaaki Tsuruoka

Recently, perovskite semiconductors have attracted much attention because of their optical and electronic properties. Until now, development of perovskite materials has focused on lead (Pb)-based perovskites. On the other hand, there are many reports on perovskite semiconductors based on the non-toxic element tin (Sn) as an alternative material. However, the properties of Sn-based perovskites can be readily changed due to the oxidation from Sn^{2+} to Sn^{4+} state. In this study, we study the formation of Sn-based perovskite/Sn MOF ($[Sn_2(dobdc)]$) composites and the characterization of properties of the resulting composites.

Keywords : Sn perovskite semiconductor , Sn metal-organic frameworks, Nanocomposites

近年、ペロブスカイトは優れた発光特性ならびに高い光電変換効率を示すことから、LED、太陽電池、熱電変換デバイスなどにおける次世代の半導体材料として注目されている。これまで Pb をベースとしたペロブスカイト半導体を中心に開発が行われてきたが、非毒性かつ非希少元素である Sn をベースとしたペロブスカイト半導体が代替材料の一つとして検討されている。しかしながら、Sn ベースの半導体結晶は Sn^{2+} が Sn^{4+} へと酸化されやすく、特性が変化してしまうという問題点が挙げられる。このような観点から、酸化耐性に優れた Sn ベースペロブスカイト半導体の開発が盛んに行われている。そこで本研究では、$CsSnBr_3$ 半導体と Sn MOF : $[Sn_2(dobdc)]$ （dobdc: 2,5-dihydroxyterephtalate）からなる複合体の作製を行った。まず、CsBr および $SnBr_2$ を DMSO に溶解し、さらに Sn MOF を加え、真空下にて溶液を 170℃で加熱することで溶媒を揮発させる手法にて $CsSnBr_3$ の合成を行った。これにより得られた試料の XRD 測定を行ったところ、未反応物などに由来するピークも確認されるが、Sn MOF に由来するピークは確認されなかったことから、目的組成のペロブスカイトが得られており、Sn MOF が Sn の酸化を抑制していることが示唆された（図）。また SEM 観察を行った結果、$CsSnBr_3$ 結晶に由来する八面体構造の結晶が確認された。

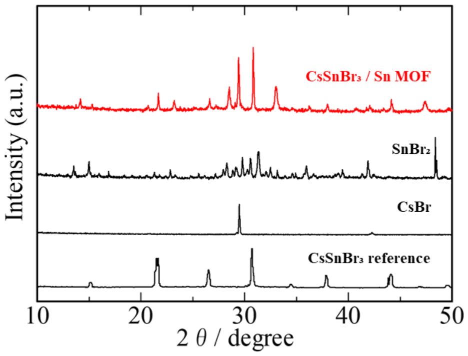


Figure. XRD pattern of the obtained sample.

サブナノ空間で発現する性質を利用した機能性材料開発

（都産技研[1]・慶大理工[2]）○林　孝星[1]・渡辺　洋人[2]・今井　宏明[2]

Development of functional materials utilizing properties exhibited in sub-nanoscale spaces

([1]*Tokyo Metropolitan Industrial Technology Research Institute*, [2]*Faculty of Science and Engineering, Keio University*) ○Kosei Hayashi,[1] Hiroto Watanabe,[2] Hiroaki Imai[2]

In recent years, development of a functional material using a material having a nano space has attracted attention. Since various substances taken into the nano-space show physical properties different from those in the bulk state, they are likely to show novel characteristics. The porous silica (super microporous silica, SMPS) we have developed has a pore size of around 1 nm, heat resistance, and visible light transmission. Using SMPS, we have been developing functional materials such as catalyst carriers1) and fluorescent materials2). It was suggested that within the pores of SMPS, not only are molecules supported in isolation, but strong hydrogen bonds, which can only be formed within SMPS, are also involved3). By utilizing this property, it becomes possible to change the energy levels of molecules as well as to immobilize and stabilize molecular structures (Figure 1). This study reports on previous development of functional materials utilizing this property.

Keywords：Porous Silica gel; Nanoscale Spaces; Hydrogen Bonds; Stable Immobilization

近年、ナノ空間を利用した機能性材料の開発が注目されている。ナノ空間に取り込まれた様々な物質はバルク状態とは異なる物性を示すため、新奇な特性を示す可能性が高い。我々が開発した多孔質シリカ（スーパーマイクロポーラスシリカ、以下 SMPS）は 1 nm 前後の細孔径、耐熱性、可視光透過性を有している。SMPS を利用して、触媒担体1)や蛍光材料2)といった機能性材料開発を行ってきた。特に SMPS 細孔内では、分子の孤立担持のみではなく、SMPS 内でのみ形成可能な強い水素結合が関与していることが示唆された3)。この性質を利用すると、分子のエネルギー準位を変えることや分子構造を固定化し安定化させることが可能となる（図１）。本研究はこの性質を利用したこれまでの機能性材料開発について報告する。

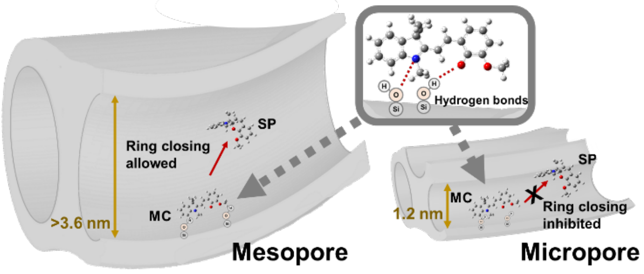


図１　フォトクロミック分子のシリカ細孔内における安定固定化

1) R. Kitamura, H. Watanabe, Y. Oaki, H. Imai, *Langmuir*, **2019**, *35*, 5594.
2) K. Hayashi, S. Ogawa, H. Watanabe, Y. Fujimaki, Y. Oaki, H. Imai, *Bull. Chem. Soc. Jpn.*, **2019**, *92*, 1170.
3) K. Hayashi, Y. Fujimaki, K. Mishiba, H. Watanabe, H. Imai, *Chem. Commun.*, **2021**, 57, 13150.

Fabrication of Fluorinated Polymer Hybrid Materials with Highly Fluorinated POSS Fillers for Reducing the Refractive Index

(*Graduate School of Engineering, Kyoto University*) ○Tatsuaki Kunimitsu, Masayuki Gon, Kazuo Tanaka

Keywords: POSS; Fluorinated polymer; Organic–inorganic hybrid material; Fluorine; PFAS

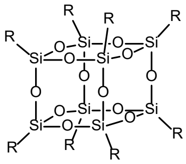


Figure 1. Chemical structure of POSS.

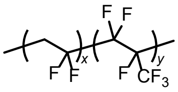


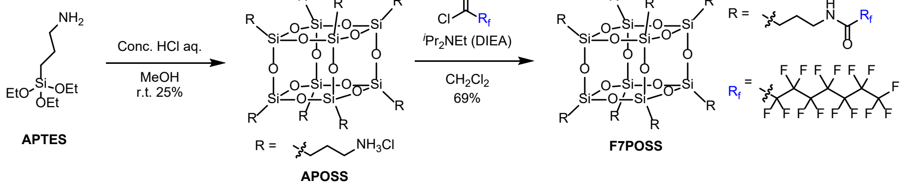
Figure 2. Chemical structure of PVDF-HFP.

Fluorinated polymers have a low refractive index and play a significant role in optical fibers and antireflective coatings, and further reduction of the refractive index is desired to improve the performance of the fluorinated polymers. The refractive index and chemical structure are related by the Lorentz-Lorenz equation, and the low refractive index property is achieved by a low molecular refraction derived from the fluorine atom and a large molar volume originating from the molecular structure. Since fluorinated polymers already have a remarkably high fluorine content, creating space in the material should be effective for reducing the refractive index. Herein, we propose an approach using fillers, which can tune the physical properties by the content of the fillers. On the other hand, fluorinated polymers are insoluble in common organic solvents and incompatible with other materials, which hinders the possibility of controlling physical properties with additives.

By focusing on the structural features of polyhedral oligomeric silsesquioxane (POSS) (Figure 1), we have demonstrated that POSS can be used as a filler owing to its cubic structure that exhibits durability unique to inorganic materials and its high compatibility with polymers derived from organic substituents at eight vertices.[1] When a skeleton with such a bulky structure can be placed in a fluorinated polymer, it is expected to promote the reduction of the refractive index because of its looser packing of the material. In addition, as for the problem of fluorinated polymers being difficult to mix with other materials, the substituents at the eight vertices of POSS can be used to increase compatibility.

In this study, we synthesized POSS fillers with high fluorine content (**F7POSS**) to further lower the refractive index of fluorinated polymers. **F7POSS** was mixed with a fluorinated polymer, PVDF-HFP (Figure 2), to fabricate a freestanding film. The results of refractive index measurements of the freestanding films showed that their refractive indices were reduced to $n = 1.3787$ from pristine PVDF-HFP film ($n = 1.4236$) depending on the filler content. We confirmed the usefulness of **F7POSS** as a filler for reducing the refractive index.

Scheme 1. Synthesis of **F7POSS**



[1] Tanaka, K.; Adachi, S.; Chujo, Y. *J. Polym. Sci. A Polym. Chem.* **2010**, *48*, 5712–5717.

かご型シルセスキオキサンの分子内の空孔を利用した気体分離膜の開発

（東理大創域理工 [1]・産総研 [2]）○小川　悠 [1]・五十嵐　正安 [2]・山本　一樹 [1]・郡司　天博 [1]

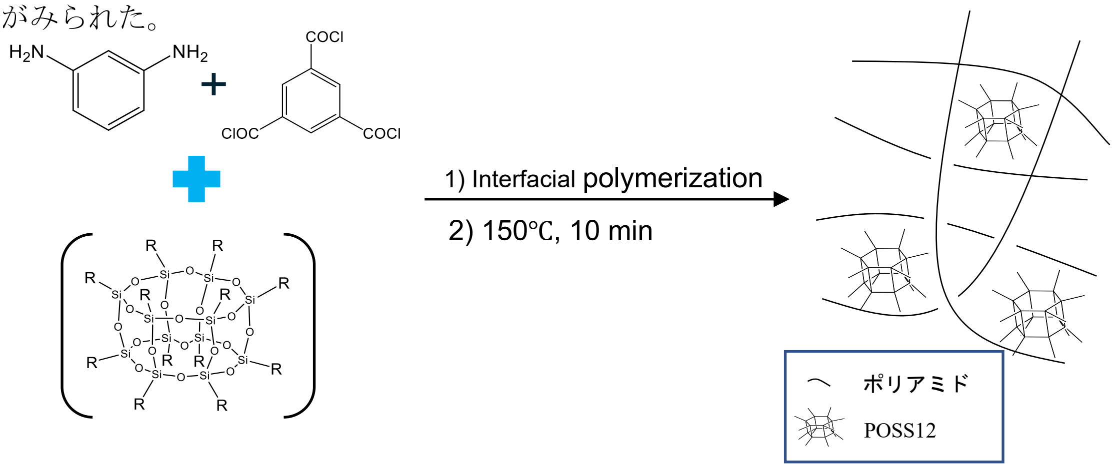
Development of gas separation membranes utilizing intramolecular vacancies in caged silsesquioxanes ([1]*Faculty of Science and Technology, Tokyo University of Science,* [2]*AIST*)

○Haruki Ogawa[1], Masayasu Igarashi[2], Kazuki Yamamoto[1], Takahiro Gunji[1]

Inorganic gas separation membranes are membranes that separate only small molecular size gases from a gas mixture mainly by molecular sieving. Among them, sodalite (SOD) zeolite membranes have been reported to selectively permeate hydrogen and helium, and the silicon six-membered ring (POSS12) in the siloxane bond of the SOD zeolite structure is considered effective for hydrogen and helium permeation. In this study, caged silsesquioxane, a molecule with the same six-membered silicon ring as the SOD zeolite structure, was added to polyamide film and deposited on the film, and a gas separation membrane was prepared and investigated in which hydrogen selectively permeates through the caged molecules. As a control experiment, polyamide membranes containing caged silsesquioxane with silicon four-membered rings (POSS8) were also prepared. The H_2/N_2 selectivity increased from 2.360 to 2.581 for the polyamide film with no additives and the film with POSS8 (5 wt%).

Keywords : POSS, gas separation, polyamide membrane

無機系のガス分離膜は、主に分子ふるいにより混合ガスから小さい分子径のガスだけを分離する膜である。なかでもソーダライト(SOD)ゼオライト膜は、水素やヘリウムを選択的に透過すると報告されており、SOD ゼオライト構造のシロキサン結合のケイ素 6 員環(POSS12)が水素・ヘリウム透過に有効とされている [1)]。本研究では、SOD ゼオライト構造と同じケイ素 6 員環を有する分子であるかご型シルセスキオキサンをポリアミド膜に添加して成膜し、かご分子の内部を水素が選択的に透過する気体分離膜の作成と調査を行った。また、コントロール実験としてケイ素 4 員環(POSS8)を有するかご型シルセスキオキサンを含むポリアミド膜を作成した。無添加のポリアミド膜と POSS8(5 wt%)を添加した膜では添加した膜のほうが H_2/N_2 の選択性が 2.360 から 2.581 への向上がみられた。



1） O. Eterigho-Ikelegbe, S.O.Bada, M.O.Daramola, *Membranes* **2020**,10,312

ヘキシル基を側鎖とするポリシルセスキオキサンの合成と非溶媒誘起相分離膜の作製

（東理大創域理工）・〇冨澤 優・山本 一樹・郡司 天博

Synthesis of polysilsesquioxanes with hexyl groups as side chains and preparation of non-solvent induced phase separation membranes

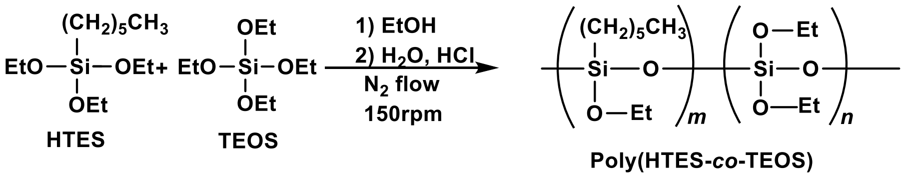
(*Graduate School of Science and Technology, Tokyo University of Science*) 〇 Yu Tomizawa, Kazuki Yamamoto, Takahiro Gunji

Inorganic ultrafiltration membranes can remove viruses and proteins and are resistant to cleaning chemicals, but they are also expensive and require multiple processes. The NIPS methods, which induces phase separation by incorporating a non-solvent (water), can be used with polysiloxane to fabricate inorganic porous membranes easily. However, the membranes are hard and easily cracked. In this study, we aim to fabricate flexible membranes by using copolymers of HTES (hexyltriethoxysilane) and TEOS (tetraethoxysilane),which have long side chains of organic groups and the NIPS method.

By varying the ratio of HTES to TEOS and the molar ratio of water to silicon, membrane was produced, in which the viscous polymer does not peel off from the substrate when immersed in water. Increasing the molar ratio of water to silicon improves the viscosity and prevents cracking, while increasing the ratio too much is known to cause wrinkling on the film surfase. When the polymer was aged immediately after synthesis at room temperature for several days before deposition, the cross-sectional SEM images the membrane had a porous structure. *Keywords : siloxane; membrane; immersion; hexyltriethoxysilane; non-solvent induced phase separation*

無機系限外ろ過膜はウイルスやタンパク質を除去でき、洗浄に用いる薬品に強い一方で、高コスト・多工程という課題をもつ。そこで非溶媒（水）の取り込みにより相分離を誘起するNIPS法をポリシロキサンに用いることで無機系多孔膜を簡便に作製できるが、膜が硬く割れやすい問題がある。本研究では、有機基の側鎖が長いHTES(ヘキシルトリエトキシシラン)とTEOS(テトラエトキシシラン)の共重合体からNIPS法により成膜することで、柔軟性を有する多孔質膜の作製を目的としている。

HTESとTEOSのモル比やケイ素に対する水のモル比を変化させていくことで、水に浸漬させた際にポリマーが基板から剥がれない、粘性を有する高分子膜（重量平均分子量10,000）を作製した。ケイ素に対する水のモル比を増やすと粘度が上昇しクラックは発生しなくなるが、増やしすぎると膜の表面にしわが寄ることが分かった。また、合成直後のポリマーを室温で数日間agingさせてから成膜すると、断面SEMから多孔質構造が確認できた。



ブテン・ブチン架橋型アルコキシシランの合成と逆浸透膜の調製

（東理大院創域理工[1]）○相澤 康太[1]・山本 一樹[1]・郡司 天博[1]

Synthesis of butene-butyne- bridged alkoxysilanes and preparation of reverse osmosis membranes

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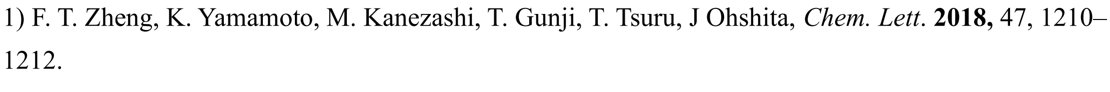
Water treatment using reverse osmosis membranes is a major seawater desalination technology, and reverse osmosis membranes using organically bridged alkoxysilanes have attracted attention due to their heat and chlorine resistance. Among them, BTESE2 and BTESE3 bridged with ethenyl and ethynyl, respectively, have been reported to have high water permeability. In this study, we synthesized butene and butyne bridged alkoxysilanes (BTESB2 and BTESB3) with increased carbon numbers to investigate their physical properties and to improve water permeability, and evaluated reverse osmosis membranes using these materials. BTESB2 was obtained from *trans*-1,4-dichloro-2-butene and trichlorosilane in 39% yield, and the reverse osmosis membrane using BTESB2 showed a water permeance of 1.2×10^{-13} m^3/(m^2・Pa・s) and a NaCl rejection of 98 %. However, the water permeation rate was lower than that of BTESE2. This is because the molecular chains became more flexible and the contribution of the molecular sieve mechanism to permeation was reduced.

Keywords：Reverse osmosis membranes; Alkoxysilanes;

逆浸透膜による水処理は主要な海水淡水化技術であり、耐熱性、耐塩素性の観点から有機架橋型アルコキシシランを用いた逆浸透膜が注目されている1)。中でも、エテニル、エチニルで架橋された BTESE2, BTESE3 は水透過性が高いことが報告されている。そこで本研究では、物性の調査と透水性の向上を目的として炭素数を増加させたブテン・ブチン架橋型アルコキシシラン(BTESB2, BTESB3)の合成とそれを用いた逆浸透膜の評価を目的とする。

BTESB3 は合成を試みたが反応の進行は確認されたものの単離が困難であった。BTESB2 は *trans*-1,4-dichloro-2-butene とトリクロロシランから収率 39%で得た(下図)。BTESB2 から作製した逆浸透膜は水透過速度が 1.2×10^{-13} m^3/(m^2・Pa・s)、NaCl 阻止率は 98 %であり、脱塩性能を示したが BTESE2 よりも水透過速度は低かった。これは分子鎖が柔軟になり明確な細孔に基づく分子ふるい機構による透過の寄与が低下したためだと考えられる。



1) F. T. Zheng, K. Yamamoto, M. Kanezashi, T. Gunji, T. Tsuru, J Ohshita, *Chem. Lett*. **2018,** 47, 1210–1212.

ホウ素触媒を用いたポリシルセスキオキサン膜の硬化

(東理大創域理工[1]) ○佐藤 春翔[1] ・山本 一樹[1] ・郡司 天博[1]

Curing of polysilsesquioxane films using boron catalyst

([1]*Faculty of Science and Technology, Tokyo University of Science*) ○Haruto Sato [1], Kazuki Yamamoto [1], Takahiro Gunji [1]

Polysilsesquioxane is a generic term for a three-dimensional crosslink of an organic chain and a siloxane bond to a silicon atom and is widely used as an organic-inorganic hybrid material because of its properties. In this study, a boron catalyst is used as a curing catalyst for polysiloxane, and the Piers-Rubinsztajn reaction), a decarbonation condensation of hydrosilane and alkoxysilane, is used to achieve excellent materials.

Triethoxysilane and vinyltriethoxysilane were used as starting materials, and copolymers (M_w around 10000) were synthesized by sol-gel method by changing the composition ratio. A boron catalyst was added to the resulting sol solution, and a freestanding film was prepared by heating and drying. Evaluation methods included FT-IR and TG-DTA measurements. When 0.1 mol% boron catalyst was added to the polymer, the ceramic yield increased from 75 % to 90 %, suggesting the progress of the PR reaction.

Keywords: Polysilsesquioxanes, Boron catalyst, Piers-Rubinsztajn reaction

ポリシルセスキオキサンは、ケイ素原子に一つの有機鎖と主鎖のシロキサン結合が三次元架橋したものの総称で、高い耐熱性や強度を有することに加えて種々の有機基を導入することで物性を変えられるため有機−無機ハイブリッド材料として広く用いられる。本研究ではポリシロキサンの硬化触媒としてホウ素触媒（トリスペンタフルオロフェニルボラン）を使用し、ヒドロシランとアルコキシシランの脱炭素縮合である Piers-Rubinsztajn(PR)反応を利用して優れた材料を目指した。

出発原料としてトリエトキシシランとビニルトリエトキシシランを用い、組成比を変更してゾル・ゲル法により共重合体（M_wは 10000 程度）を合成した。得られたゾル溶液にホウ素触媒を添加し、加熱乾燥することで自立膜を作製した。評価方法としては FT-IR や TG-DTA 測定などを行い、ポリマーに対して 0.1 mol%のホウ素触媒を添加したところセラミック収率が 75 %から 90 %に増加したことから PR 反応の進行が示唆された。

表面修飾ナノシートを用いた超撥水コーティングの作製

（慶大理工 [1]・岡山大基礎研 [2]）○須藤悠文 [1]・仁科勇太 [2]・今井宏明 [1]・緒明佑哉 [1]
Superhydrophobic coatings based on the surface-modified nanosheets ([1]*Keio University*, [2]*Okayama University*) ○Hisafumi Sudo,[1] Yuta Nishina,[2] Hiroaki Imai,[1] Yuya Oaki[1]

Exfoliated nanosheets are used as building blocks to organize higher-ordered architectures. Our group has prepared the functional coatings based on the surface-modified nanosheets exfoliated from the layered organic-inorganic composites.[1,2] In the present study, the morphology of the coating was controlled using four types of nanosheets: tetradecylamine-modified clay (C$_{14}$-clay), graphene oxide (C$_{14}$-GO), and titanate with large (C$_{14}$-TiO$_2$(L)) and small lateral sizes (C$_{14}$-TiO$_2$(S)). Drop casting of the C$_{14}$-GO and C$_{14}$-Clay nanosheets thinner than 10 nm formed a flat surface exhibiting the noniridescent structural color (Fig. 1a). Spray coating of the C$_{14}$-TiO$_2$(L) and C$_{14}$-TiO$_2$(S) thicker nanosheets provided a rough surface exhibiting high hydrophobicity (Table 1). Based on these results, the superhydrophobic surface with the contact angle 153.9 ° was obtained by coating of the C$_{14}$-GO, C$_{14}$-TiO$_2$(S), and reduced graphene oxide (rGO) nanosheets (Fig. 1b).

Keywords : Exfoliation, Nanosheets, Coating, Hydrophobic, Surface

はく離ナノシートはナノスケールのビルディングブロックとして注目を集めている。当研究グループでは、層状有機無機複合体のはく離により合成した表面修飾ナノシートを用い、コーティングを作製している [1,2]。本研究では、テトラデシルアミンを修飾したクレイ(C$_{14}$-Clay)、酸化グラフェン(C$_{14}$-GO)、大小 2 種類のチタン酸 (C$_{14}$-TiO$_2$(L), C$_{14}$-TiO$_2$(S))の合計 4 種類のナノシートを用いてコーティング表面形態の制御を試みた。厚さ 10 nm 以下の薄いナノシートである C$_{14}$-Clay と C$_{14}$-GO をドロップキャスティングすると、平滑な表面ができ、角度依存性のない構造色が現れた(Fig. 1a)。一方、厚さ 10 nm 以上の厚いナノシートである C$_{14}$-TiO$_2$(L)と C$_{14}$-TiO$_2$(S)をスプレーコーティングすると、ラフな表面ができ、高撥水性を示す膜が得られた(Table 1)。この結果を応用し、薄い C$_{14}$-GO と厚い C$_{14}$-TiO$_2$(S)ナノシート、横幅サイズが大きい還元型酸化グラフェン(rGO)を組み合わせて接触角 153.9 °の超撥水膜を得た(Fig. 1b)。

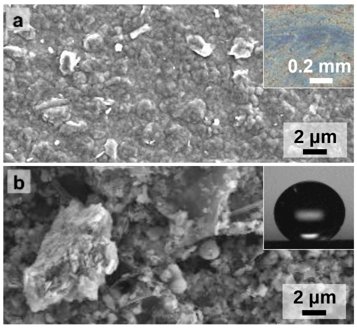


Fig. 1　a) C$_{14}$-Clay 構造色膜. b) 接触角 153.9 °の超撥水膜.

Table 1　4 種類のナノシートの厚さとそのコーティングの接触角および構造色.

ナノシート	厚さ / nm	Spray coating 接触角・構造色	Drop casting 接触角・構造色
C$_{14}$-Clay	4.4 ± 2.4	75.0 °・無	78.6 °・有 [a]
C$_{14}$-GO	4.0 ± 3.2	95.9 °・無	106.5 °・有 [a]
C$_{14}$-TiO$_2$ (L)	14 ± 17	127.6 °・無	111.1 °・無
C$_{14}$-TiO$_2$ (S)	17 ± 20	139.9 °・無	127.4 °・無

[a] 角度依存性なし.

1）R. Hikichi, Y. Tokura, Y. Igarashi, H. Imai, Y. Oaki, *Bull. Chem. Soc. Japan*, **2023**, *96*, 8.
2）Y. Haraguchi, H. Imai, Y. Oaki, *Adv. Mater. Interfaces* **2022**, *9*, 2201111.

窒化ホウ素を充填したポリスチレンの熱物性評価

（阪大レーザー研[1]）○本多 巧一[1]

Thermal Properties of Polystyrene Loaded with Boron Nitride Filler

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Loading polymer with boron nitride (BN) produces composite material with improved thermal conductivity over the polymer. Since both materials have high electrical resistance, this composite material can be an insulating thermal conductor. The relationship between filler fraction and thermal properties is important in material design. Some studies have been conducted to evaluate the effect of BN filler fraction on the thermal conductivity of the composite [1, 2]. However, these studies have not necessarily elucidated the relationship due to uncertain factors such as the effects of pretreatment and additives. In this study, a composite of BN and polystyrene was prepared by kneading styrene, polystyrene, BN, and initiator (<1 wt%) directly without any pretreatment to a paste, which was then heated to cure. For materials with filler fractions of 40-65 wt%, the thermal conductivity of these materials was measured by the laser flash method. The results indicated the thermal conductivity increased with an increasing filler fraction.

Keywords : Composite Material; Boron Nitride; Polystyrene; Thermal Conductivity

高分子に窒化ホウ素(BN)を充填すると、高分子の熱伝導率が向上する。さらに、両者は電気抵抗が大きい材料であることから、この複合材料は絶縁性の熱伝導材料となりうる。フィラー充填率と熱物性の関係は材料設計上重要であり、BN フィラー充填率が複合材料の熱物性に与える影響を評価する研究が行われている[1,2]。しかしこれらの研究では、材料の前処理や添加物の影響などの不確かな要因があることから、統一的な理解には至っていない。

本研究では、前処理なくスチレンとポリスチレン、BN、少量の重合開始剤（全重量に対して 1wt%未満）をペースト状になるまで練和し、これを加熱重合することで BN とポリスチレンを複合化した硬化物を作製した。レーザーフラッシュ法によりフィラー充填率 40～65 wt%の硬化物の熱伝導率を測定したところ、フィラー充填率の増大に伴い熱伝導率が上昇したことが確認された。

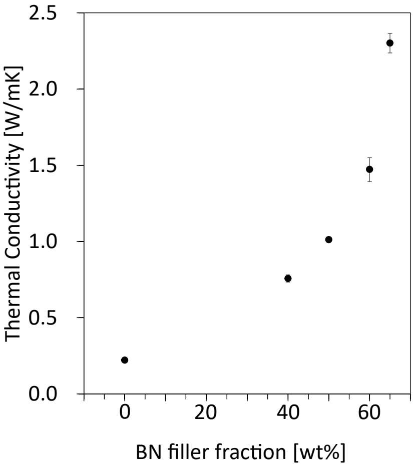

Fig. 1 Thermal conductivity of the BN/polystyrene composite as a function of filler fraction. Markers and error bars indicate averages and standard errors of 8 samples, respectively.

1) Z. Wang, et al., *IEEE Transactions on Dielectrics and Electrical Insulation* **2011**, *18*, 1963.
2) V. M. Samoilov, et al., *Russian Physics Journal* **2022**, *65*, 80.

ポリブチレンテレフタレート（PBT）をハードセグメントとした熱可塑性エラストマーへの酸化亜鉛をバインダー層とした表面処理法の開発

（宇都宮大[1]・日本プレーテック[2]）吉原佐知雄[1]，大田和 幸香[1]，中澤育子[1]，石川祥久[2]，元井 健一郎[2],及川 哲史[2], Development of a surface treatment method using zinc oxide as a binder layer for thermoplastic elastomers with PBT as a hard segment ([1]*Faculty of Engineering, Utsunomiya University*, [2] *Nippon Platec Co. Ltd.,*) ○[1]Sachio YOSHIHARA, [1]Yukika OTAWA, [1]Ikuko NAKAZAWA, [2] Yoshifusa ISHIKAWA, [2] Kenichiro MOTOI, [2] Tetsushi OIKAWA

In this study, we examined a versatile plating pretreatment method for various engineering plastics by catalyzing a zinc oxide thin film generated by electroless deposition with a palladium acid solution and applying electroless nickel to the surface.

The plating pretreatment method employed in this study was able to confirm the generation of a plating film with high adhesion at thermoplastic elastomers, which has a large hard segment ratio. On the other hand, for thermoplastic elastomers, which has a large soft segment ratio, it is necessary to improve adhesion. On the other hand, in electroless nickel plating by the conventional method, plating is difficult to plate on the substrate used in this study, or a plating film with low adhesion is generated. From the above, it seems that nickel plating has progressed well by zinc oxide by electroless deposition and catalyzing.

Keywords：Zinc oxide, binder layer, Thermoplastic elastomers, PBT, Hard segment

本研究では、無電解により生成した、酸化亜鉛薄膜をパラジウム酸溶液にて触媒化し、表面に無電解ニッケルを行うことで、様々な熱可塑性エラストマーに対して、汎用性のあるめっき前処理法を検討した。

本研究で採用しためっき前処理法は、ハードセグメント比が多い熱可塑性エラストマーで密着力が高いめっき膜の生成が確認できた。その一方で、ソフトセグメント比が多い熱可塑性エラストマーに関しては、密着性の改善が必要である。

一方、従来法による無電解ニッケルめっきでは、本研究で用いている基板に対してはめっきが困難、もしくは密着性の低いめっき皮膜が生成してしまう結果となった。

以上のことから無電解めっきにより酸化亜鉛を析出させ[1)]、触媒化を行うことでニッケルめっきが良好に進んだものとみられる。本手法は従来のクロム酸等によるエッチングに弱い基板に対しても有効と思われ、さらに平滑接続が可能という汎用性の高い手法と考えられ、現在、PS, PET, PEEK 材等への適用を試みている。

1) Masanobu Izaki and Takashi Omi; *J. Electrochem. Soc.* , **144**, L3,1997.

生分解性高分子/水酸アパタイト複合体の表面修飾(I) －エチドロン酸の導入検討－

（上智大理工[1]）○伊藤 凜[1]・藤田 正博[1]・陸川 政弘[1]・竹岡 裕子[1]

Surface modification of biodegradable polymer/hydroxyapatite complex (I) –Introduction of etidronic acid–

([1] *Faculty of Science and Technology, Sophia Univ.*) ○Rin Ito,[1] Masahiro Fujita,[1] Masahiro Rikukawa,[1] Yuko Takeoka[1]

Composites of poly(L-lactic acid) (PLLA) and hydroxyapatite (HAp) show excellent biocompatible and mechanical properties, while the weak binding at the organic-inorganic interface and the low material strength are problems. In this study, etidronic acid, a bisphosphonate compound with chelating ability, was introduced as an interface modifier to evaluate its modifying ability on HAp and its influence on the strength of the composites. The FT-IR results show the shift derived from phosphonic acid group of etidronic acid at E-HAp modified with 0.1 M and 0. 5M etidronic acid aq. solutions at room temperature. The chelate formation between etidronic acid and Ca ions in HAp was suggested. Since the weight loss rate at 500 ºC suggested excessive modification due to physical adsorption at 0.5 M, PLLA/E-HAp composites were fabricated using 0.1 M solutions. There was a slight increase in the toughness of PLLA/E-HAp compared to PLLA/HAp, suggesting the effect of the interface modifier.

Keywords : Hydroxyapatite; Poly(l-lactic acid); Chelate

生分解性高分子であるポリ(L-乳酸)(PLLA)と水酸アパタイト(HAp)からなる複合体は優れた生体適合性と機械的特性を示す一方で、PLLA と HAp の界面の結合が弱く、材料強度が低いことが課題である。本研究では、キレート能を有するビスホスホネート化合物であるエチドロン酸を界面修飾剤に用い、HAp への修飾能、及び PLLA/HAp 複合体の強度への影響を評価した。図 1 に 0.1 と 0.5 M のエチドロン酸水溶液を用いて室温で HAp を修飾した E-HAp、エチドロン酸、HAp の FT-IR スペクトルを示す。E-HAp では HAp に起因する 1190-960 cm^{-1} の伸縮振動ピークに加え、エチドロン酸のホスホン酸基由来の伸縮振動が単体と比較して低波数に観察された。HAp 中の Ca とエチドロン酸間でのキレート形成が示唆された。熱重量分析の結果、0.5 M では物理吸着による過剰な修飾が示唆されたため、0.1 M 溶液を用いて PLLA/E-HAp 複合体を作製した。三点曲げ試験の結果、PLLA/E-HAp 複合体の靭性は PLLA/HAp 複合体と比較してわずかに増加した。

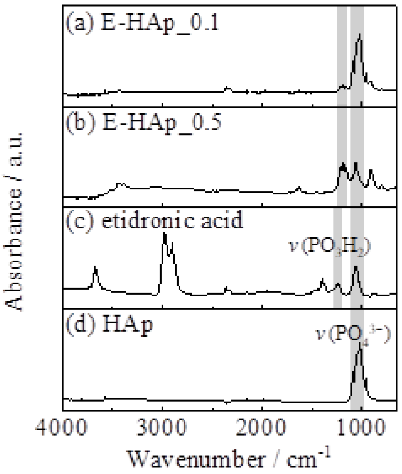

Figure 1. FT-IR spectra of E-HAp prepared at r.t. by using (a) 0.1 M and (b) 0.5 M etidronic acid aq. solution, (c) etidronic acid, and (d) *p*-HAp.