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

Tue. Mar 19, 2024 1:00 PM - 3:40 PM JST | Tue. Mar 19, 2024 4:00 AM - 6:40 AM UTC C442(442, Bldg. 4 [4F])

[C442-2pm] 20. Materials Chemistry -Basic and Application-

Chair: Yoshimasa Amano, Yoshiumi Kohno

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[C442-2pm-01]

Important foctors related to printability of paste containing inorganic particles

○Tatsuo Aikawa[1] (1. Sumitomo Metal Mining Co., Ltd.)

Japanese
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[C442-2pm-02]

Synthesis of partially silylated form using $Q_8{}^H$

○Naoya Okamura[1], Kazuki Yamamoto[1], Masayasu Igarashi[2], Takahiro Gunji[1] (1. Fac. of Sci. and Tech., Tokyo Univ. of Sci., 2. AIST)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[C442-2pm-03]

Synthesis and Characterization of Polyhedral Oligomeric Silsesquioxane with Vinylazulene in the Side Chain

○Nao Fukuta[1], Kazuki Yamamoto[1], Takahiro Gunji[1] (1. Fac. of Sci. and Tech., Tokyo Univ. of Sci.)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[C442-2pm-04]

Adsorption of nitrate ions in aqueous phase promoted by *N*-methylation of pyridinic nitrogen on flame-resistant polyacrylonitrile (PAN) fiber.

○Masahiro Fukuhara[1], Yoshimasa Amano[2,3], Motoi Machida[2,3] (1. Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Chiba University, 2. Graduate School of Engineering, Chiba University, 3. Safety and Health Organization, Chiba University)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[C442-2pm-05]

Development of sustained release materials for antioxidant depending on the surrounding circumstances

○Atsuya Toyoshima[1], Daiyu Kodama[2], Yoshiumi Kohno[3] (1. Graduate Schook of Engineering, Shizuoka University, 2. Kamiya Riken Co., 3. School of Engineering, Shizuoka University)

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[C442-2pm-06]

Electrochromic reaction on polystyrene nanoparticle-modified electrode showing structural color

○Hayata Shirai[1], Momona Yamaguchi[1], Norihisa Kobayashi[1], Kazuki Nakamura[1] (1. The Univ. of Chiba)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

Break

🏷 English
2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

[C442-2pm-07]

Differences in the stability enhancement of several types of anthocyanins intercalated into montmorillonite

○THU ANH NGUYEN[1], Yoshiumi Kohno[1], Masashi Shibata[2], Ryo Watanabe[1], Choji Fukuhara[1] (1. Shizuoka University, 2. Tokyo University of Technology)

🏷 Japanese
2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[C442-2pm-08]

Preparation of Organic-Inorganic Hybrid Porous Membranes by Non-Solvent Induced Phase Separation Method

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

🏷 Japanese
2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[C442-2pm-09]

Water separation propaties of organic- inorganic hybrid membranes using POSS dendrimers as fillers

○Misaki Yoshida[1], Kazuki Yamamoto[1], Takahiro Gunji[1] (1. Tokyo University of Science, the Faculty of Advanced Science and Engineering)

🏷 Japanese
2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[C442-2pm-10]

Preparation and evaluation of organic-inorganic hybrid reverse osmosis membrane added with cage-type siloxane having hydroxyl groups

○Rika Nagai[1], Kazuki Yamamoto[1], Takahiro Gunji[1] (1. Tokyo University of Science, Faculty of Advanced Science and Engineering)

🏷 Japanese
2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

[C442-2pm-11]

Synthesis of titanium phosphonate clusters and the evaluation of their photocatalytic performance

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

🏷 Japanese
3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[C442-2pm-12]

Development of Fluorinated Polymer Hybrid Materials with Highly Fluorinated POSS Fillers

○Tatsuaki Kunimitsu[1], Keisuke Shibahara[2], Masayuki Gon[2], Kazuo Tanaka[2] (1. Kyoto Univ., 2. Grad. Sch. of Eng., Kyoto Univ.)

🏷 English
3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC

[C442-2pm-13]

Powderization of Gallium-Indium Eutectic Liquid Metal and Application to the Development of Functional Hybrids

○Christopher Hiromi Shimamura[1], Shunichiro Ito[1], Kazuo Tanaka[1] (1. Kyoto University)

🏷 Japanese

3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC

[C442-2pm-14]

Reverse osmosis membrane based on organic cross-linked polysilsesquioxane with polyacrylic acid

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

🏷 Japanese

3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC

[C442-2pm-15]

Stability evaluation of perovskite thin films by machine learning

○Ryo Fukasawa[1], Toru Asahi[1], Takuya Taniguchi[2] (1. Graduate School of Advanced Science and Engineering, Waseda University, 2. Center for Data Science, Waseda University)

無機粒子含有ペーストの印刷性に関わる要素

（住友金属鉱山株式会社 [1]） ○相川 達男 [1]

Important factors related to printability of paste containing inorganic particles

([1]*Materials laboratories, Sumitomo Metal Mining, Co., Ltd.*) ○Tatsuo Aikawa [1]

Pastes containing conductive particles are essential materials for manufacturing printable electronics. In such usage, the pastes are used by printing on substrates. In this study, we discuss the viscosity and particle separability of the paste as important factors related to printability. The general components of a paste are shown in Fig. 1. Solvents, binder resins, and additives are included as organic materials, and metal and ceramic particles are used as inorganic particles. Our research group has found that the adsorption of the binder resin to the particles is an important factor in adjusting the viscosity of the paste. Viscosity in the low shear rate region varied depending on the amount of binder resin adsorbed, which should be related to the smoothing of the paste surface after paste printing. Several types of particles may be used in the paste. However, difference in size and/or specific gravities of the particles may cause separation of these particles in the paste. Our research group has also found that the degree of the separation is related to the solubility of the binder resin in the solvent.

Keywords ：pastes, printable electronics

導電性粒子を含むペーストは、プリンタブルエレクトロニクスを製造する上で必須の材料となる。このようなペーストは基板上に印刷し使用され、精密に印刷される必要がある。本研究では、印刷性に関連する要素として、ペーストの粘度や粒子分離性の調整の仕方について議論する。

ペーストの一般的な構成要素は Fig.1 のようになる。有機物として、溶剤、バインダー樹脂、添加剤が含まれ、無機粒子には金属粒子やセラミック粒子が使用される。印刷のしやすさはペーストの粘度が関連している。ペーストの粘度を調整するうえで、バインダー樹脂の粒子に対する吸着が重要であることを当社の研究グループでは明らかにしている。特に低せん断速度領域における粘度はバインダー樹脂の吸着量に依存して変化していた。低せん断速度域の粘度は、ペースト印刷後にペースト表面の平滑化に関連すると考えられ、印刷膜の表面平滑度を制御する上で、樹脂の吸着量を調整することが重要であると言える。

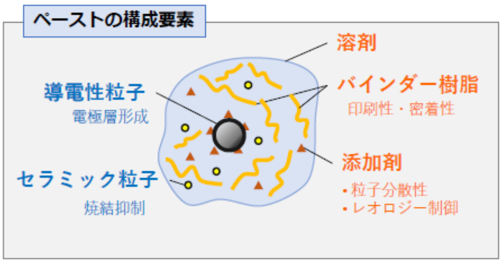


Fig.1. General components of paste for manufacturing electronics.

またペーストには 2 種類以上の粒子を使用することがある。互いにサイズや比重が異なる粒子を用いる場合、ペースト中で互いに分離することがあり所望の特性を得ることができない。当社の研究グループでは、この分離の程度が、バインダー樹脂の溶剤に対する溶解性が関連する結果を得ており、これについても報告する。

Q_8^Hを用いた部分シリル化体の合成

（東理大創域理工 [1]・産総研触媒セ [2]）○岡村 直哉 [1]・山本 一樹 [1]・五十嵐 正安 [2]・郡司 天博 [1]

Synthesis of partially silylated form using Q_8^H

([1]*Faclyty of Science and Technology, Tokyo University of Science*, [2]*Interdisciplinary Research Center for Catalytic Chemistry*, *National Institute of Advanced Industrial Science and Technology (AIST)*) ○Naoya Okamura,[1] Kazuki Yamamoto,[1] Masayasu Igarashi,[2] Takahiro Gunji[1]

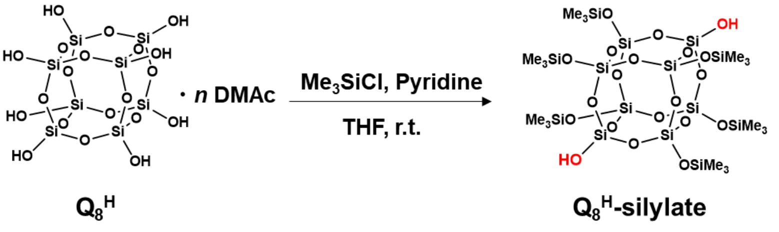
Polyhedral oligomeric silsesquioxane (POSS) is a molecule consisting of a cage framework of siloxane bond (Si-O-Si) with side chains. Recently, POSS has attracted attention as building blocks for organic-inorganic hybrids. Q_8^H 1), which has a hydroxy group as a side chain, was isolated stably for the first time in high yield. In the previous research, we reported that the POSS cross-linked polymers using Q_8^H resulted in the preparation of hard and brittle free-standing film. The hard and brittle properties of the film may be due to the random network structure of cross-linked polymers of POSS. In this study, therefore, partial silylation was performed to control the structure of Q_8^H by reducing the number of cross-linking reaction points.

Q_8^H was dissolved in THF to prepare a 2.0×10^{-2} M solution. Q_8^H was silylated with chloro(trimethyl)silane in the presence of pyridine at room temperature. After the reaction, NMR, IR, and ESI-MS revealed the formation of silylates having six or seven trimethylsilyl groups substituted for a POSS molecule.

Keywords: Siloxane; Polyhedral Oligomeric Silsesquioxanes; Organic/inorganic hybrids; Building block; Silylation

かご型シルセスキオキサン (POSS)は、シロキサン結合 (Si-O-Si)からなるかご骨格と側鎖からなる分子であり、有機-無機ハイブリッドのビルディングブロックとして注目されている。側鎖がヒドロキシ基の Q_8^H は安定的に単離できる化合物として報告されている 1)。これまでに、Q_8^Hを用いた POSS 架橋高分子の合成を行ったところ、硬くて脆い自立膜が調製された。この原因として、POSS 架橋高分子の多くがランダムなネットワーク構造を有していることが考えられる。本研究では架橋反応点を減らすことで Q_8^Hの構造制御を目的として、部分シリル化を行ったので報告する。

Q_8^Hを THF に溶解させ、2.0×10^{-2} M の溶液を調製した。アルゴン雰囲気下でクロロ(トリメチル)シランとピリジンを Q_8^Hに対して 4, 6, 8 当量となるように加え、室温中シリル化を行った。反応終了後、NMR, IR, ESI-MS により POSS 1 分子に対して 6-7 箇所がトリメチルシリル基で置換されたシリル化体の生成が分かった。



1) M. Igarashi, T. Nozawa, T. Matsumoto, F. Yagihashi, T. Kikuchi and K. Sato, *Nature Commun.*, **12**, 7025, 1-13 (2021).

側鎖にビニルアズレンを有するカゴ型シルセスキオキサンの合成と性質

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

Synthesis and Characterization of Polyhedral Oligomeric Silsesquioxane with Vinylazulene in the Side Chain

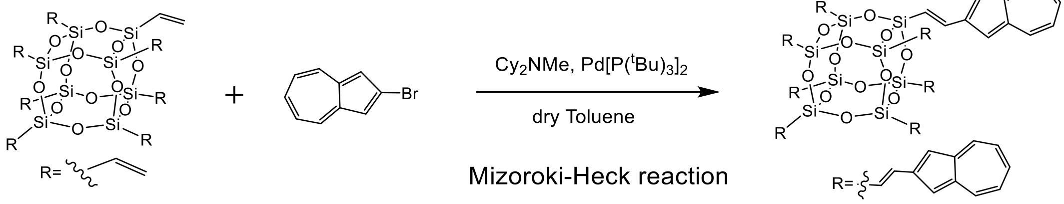
([1]*Faculty of Science and Technology, Tokyo University of Science*) ○Nao Fukuta [1], Kazuki Yamamoto [1], Takahiro Gunji [1]

Cage silsesquioxane (POSS) has attracted attention as an organic-inorganic hybrid material because of its excellent thermal and chemical stabilities derived from its siloxane bond (Si-O-Si) based skeleton and the possibility of introducing various organic substituents into the side chains. Recently, it has been reported that the introduction of an organic chromophore into the side chain of POSS causes a large red-shift in the fluorescence spectrum, which is suggested to be due to the fact that the LUMO of POSS is located at the center of the cage-structure. In this study, we report the synthesis and optical properties of azulene, a non-benzenoid with polarized structure, introduced into all side chains of POSS according to the following formula. The Mizoroki-Heck reaction of vinyl-substituted POSS with 2-bromoazulene gave a blue solid. Identification was performed by various NMR and ESI-MS measurements, and the 8-substituted compound was obtained in higher purity. The optical property of this product was also investigated by UV-Vis spectral analysis.

Keywords : POSS, Azulene, 3D conjugation, Optical Property, Mizoroki-Heck reaction

カゴ型シルセスキオキサン (POSS) は、シロキサン結合 (Si-O-Si) からなる主骨格に由来する優れた熱的、化学的安定性を示し、側鎖に様々な有機置換基を導入可能であることから有機-無機ハイブリッド材料として注目を集めている。近年、POSS の側鎖に有機発色団を導入すると蛍光スペクトルが大きくレッドシフトすることが報告され 1)、これは POSS の LUMO がカゴ骨格の中心に位置することによると示唆されている。本研究では、下式に従い、分極構造を持つ非ベンゼン系芳香族化合物であるアズレンを POSS の全ての側鎖に導入した化合物の合成及びその光学的性質を報告する。

ビニル基を置換した POSS (**1**) と 2-ブロモアズレン (**2**) の溝呂木-Heck 反応により化合物 **3** の青色固体を得た。同定は各種 NMR 及び ESI-MS 測定によって行い、高純度な 8 置換体を得た。また、UV-Vis スペクトル測定により **3** の光学的性質の調査を行った。



1 **2** **3**

1) N. R. Vautravers, P. Andre, D. Cole-Hamilton, *J. Mater. Chem.*, **19**, 4545-4550 (2009).

PAN 繊維表面のピリジン系窒素の *N*-メチル化により促進される水中の硝酸イオンの吸着

福原 誠大 [1]，天野 佳正 [2,3]，町田 基 [2,3]（1．千葉大学工学部 2．千葉大学大学院工学研究院，3．千葉大学総合安全衛生管理機構）
Masahiro Fukuhara[1], Yoshimasa Amano[2,3], Motoi Machida[2,3] (1. Faculty of Engineering, Chiba University, 2. Graduate School of Engineering, Chiba University, 3. Safety and Health Organization, Chiba University)

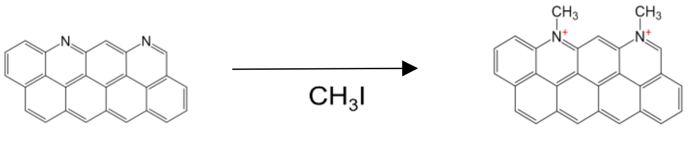
Nitrate ion contamination of soil and environmental water is currently a problem due to improper treatment of livestock excrement and excessive use of fertilizers, so there is need to remove nitrate ions. Activated carbon, which is easy to handle and design and low cost, is a widely used adsorbent. Previous studies have reported that anions such as nitrate ions were adsorbed on positively charged quaternary nitrogen (N-Q) on activated carbon fiber, whereas they repelled pyridine-type nitrogen (N-6) and pyrrole-type nitrogen (N-5), which are slightly negatively charged due to non-covalent electron pairs. In this study, we attempted to convert pyridine-type nitrogen (N-6) to quaternary nitrogen by examining the *N*-methylation conditions. Flame-resistant polyacrylonitrile (PAN) fiber with 20 wt% nitrogen content containing pyridine-type nitrogen (N-6) was treated with iodomethane and by mixing the PAN fiber in methanol for 3 days at 40°C while maintaining alkalinity. The result showed that the adsorption of the PAN fiber could be improved from 0.03 mmol/g to 0.35 mmol/g.

Keywords : *N*-methylation, Adsorption of nitrate ion, Polyacrylonitrile (PAN) fiber, Methyl iodide

現在，家畜の排泄物の不適切な処理や肥料の過剰使用により，土壌や環境水の硝酸イオン汚染が問題になっているため，硝酸イオンを除去することが求められている。硝酸イオン吸着剤として操作や設計が容易で，低コストである活性炭が挙げられる。

先行研究で，硝酸イオンのような陰イオンは炭素繊維上にある正に帯電した四級窒素（N-Q）に吸着するのに対して，非共有電子対の影響でわずかに負に帯電したピリジン型窒素 (N-6)およびピロール型窒素 (N-5)とは反発することが報告されている。

そこで本研究では，炭素繊維上にあるピリジン系窒素（N-6）を，第四級窒素に転化することを試みた。*N*-メチル化条件を検討した結果，ピリジン系窒素（N-6）を含む窒素含有量 20wt%の耐炎化ポリアクリロニトリル（PAN）繊維を，ヨードメタンとメタノール中で，アルカリ性に保ちながら 40℃の条件で 3 日間混合することで, PAN 繊維の吸着量を 0.03mmol/g から 0.35mmol/g まで向上させることができた。



ハイドロタルサイト層間へ複合化した没食子酸の周囲環境に応じた放出制御

(静大院総合科学技術[1]・神谷理研[2]・静岡大工[3]) ○豊嶋 淳也[1]・小玉 大雄[2]・河野 芳海[3]

Development of sustained release materials for antioxidant depending on the surrounding circumstances ([1]*Graduate School of Engineering, Shizuoka University*, [2]*Kamiya Riken Co,*[3]*School of Engineering, Shizuoka University*)○Atsuya Toyoshima,[1] Daiyu Kodama,[2] Yoshiumi Kohno[3]

Because antioxidant tends to be lost by self-oxidation, excess amount of antioxidant is required to conserve products for a long period. In this study, we attempted to protect the gallic acid (GA), a typical antioxidant, by intercalation into the layers of hydrotalcite (HT), a layered clay mineral with anion-exchangeable property. The aim of this study is to maintain the antioxidative effect for a long time by the slow release of GA from the HT interlayers.

The composite sample GA/HT was prepared by a conventional reconstruction method; calcined HT was added to an aqueous GA solution at pH 7. The slow-release properties were evaluated by dispersing GA/HT in water with the quantification by UV-Vis.

In the release test, the amount of GA intercalated in GA/HT decreased, suggesting that GA was released into water. A peak at 370 nm attributed to GA derivatives was observed in the eluate. Fig. 1 shows the results of the release test conducted under air and under nitrogen. The release of the GA derivative was accelerated under air, suggesting that the GA, which lost its carboxyl group due to oxidative polymerization, was released outside the layer. The release depending on the oxidative circumstances will expectedly result in a more effective and longer-lived material.

Keywords : antioxidant, composite material, gallic acid, clay, hydrotalcite

抗酸化剤は拡散や自己酸化により減少するため, 長期間の品質維持のためには過剰の添加を要する。本研究では, 抗酸化剤である没食子酸(GA)を, アニオン交換性を有する層状化合物ハイドロタルサイト(HT)の層間に複合化し, その保護を試みた。GAのHT層間からの徐放により, 長期間の酸化防止効果の持続を目指した。

焼成したHTをpH 7.0に調製したGA水溶液中に加えて撹拌・静置を行う再構築法により, 複合化試料GA/HTを調製した。GA/HTをイオン交換水に分散させてGAの放出試験を行い, UV-visで溶出挙動を評価した。

放出試験では, GA/HTに複合化されたGA量が減少したため, 液中にGAが放出されたと考えた。溶出液中にはGA誘導体に帰属される370 nmのピークが確認された。Fig. 1に大気下と窒素下で行った放出試験の結果を記載する。大気下で誘導体の放出が促進されたため, 酸化重合によりカルボキシル基を失ったGAが層外に放出されたと考えた。環境に応じた放出により, より効果的で長寿命な材料となることが期待できる。

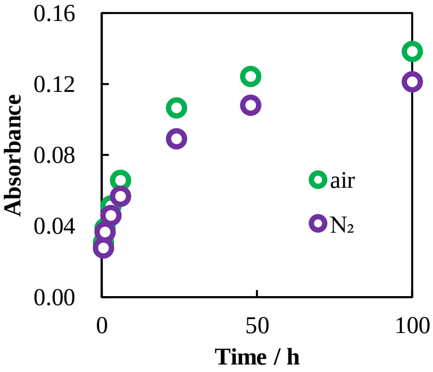


Fig. 1 Effect of the oxidative circumstances on the emission of gallic acid derivative, exhibiting absorption at 370 nm.

構造色を示すポリスチレンナノ粒子修飾電極上のエレクトロクロミック反応

（千葉大工[1]、千葉大院工[2]）○白井 颯太[1]・山口 桃奈[2]・小林 範久[2]・中村 一希[2]

Electrochromic Reaction on Polystyrene Nanoparticle-modified Electrode Showing Structural Color

([1]*Fac. Eng., Chiba Univ.*, [2]*Grad. Sch. Eng., Chiba Univ.*) ○Hayata Shirai,[1] Momona Yamaguchi,[2] Norihisa Kobayashi,[2] Kazuki Nakamura[2]

Electrochromic (EC) materials exhibit reversible color change by electrochemical redox reaction. Structural color is produced by reflecting light of a specific wavelength based on a periodic structure. We aim to create novel functional materials by combining both coloring mechanisms. In this study, polystyrene (PS) nanoparticle dispersions with an average particle size of 210 nm were modified on ITO electrodes. The PS nanoparticle-modified ITO electrodes showed greensh structural color. A electrolyte solution containing a viologen derivative (HV^{2+}), an EC material, were combined with PS nanoparticle-modified electrode. From the cyclic voltammograms of HV^{2+} by using PS nanoparticle modified electrode. Potentials for the reduction and oxidation were almost same as the case of normal ITO electrode, suggesting that PS nanoparticles and HV^{2+} can be used in the same system.

Keywords: Structural color, Opal structure, Electrochromism, Viologen derivative, Polystyrene nanoparticles

エレクトロクロミック(EC)材料は電圧印加により可逆的な色変化を示す。また構造色は周期構造によって特定波長の光を反射することで生じる色であり、光沢をもつ。我々はこれらの発色機構を組み合わせることで新規機能性材料の創成を目指している。本研究では、平均粒径 210 nm のポリスチレン(PS)ナノ粒子分散液をキャストにより ITO 電極上に修飾し、510 nm に反射ピークを有する緑の構造色を示す PS ナノ粒子修飾 ITO 電極を作製した。また炭酸プロピレン(PC)に過塩素酸テトラ-n-ブチルアンモニウムと EC 材料であるビオロゲン誘導体(HV^{2+})を溶解させた試料溶液を作製した。試料溶液に対し、作用極に PS ナノ粒子修飾 ITO 電極を用いた3極素子でサイクリックボルタンメトリー測定を行い、PS ナノ粒子の修飾の有無によるサイクリックボルタモグラムの違いを比較した。還元及び酸化開始電位が一致したことより、PS ナノ粒子修飾 ITO 電極上で HV^{2+}を EC 材料として使用可能ということが示唆された。

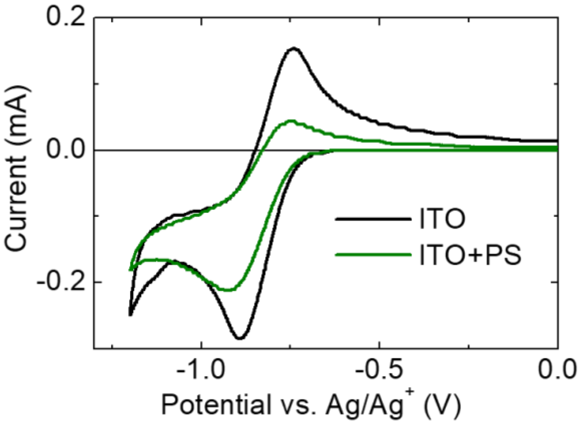


Fig1. Cyclic voltammogram of HV^{2+} using ITO electrode or ITO+PS electrode

Differences in the stability enhancement of several types of anthocyanins intercalated into montmorillonite.

([1]*Shizuoka University*, [2]*Tokyo University of Technology*) ○THU ANH NGUYEN[1], Yoshiumi Kohno[1], Ryo Watanabe[1], Choji Fukuhara[1], Masashi Shibata[2].

Keywords: Natural pigment; Clay; Sugar moiety; Composite material; Enhanced stability.

Anthocyanin (AN) is known as a water-soluble cationic pigment with less toxicity and high antioxidants that have the potential for utilization in food dyeing. However, its instability impairs consumer acceptability. The stability enhancement of AN was improved by intercalation of cationic AN into montmorillonite (cationic-exchangeable clay, KF) layers. [1] In this study, some types of anthocyanins (shown in Figure 1) were applied to prepare hybrid compounds (AN/KF).

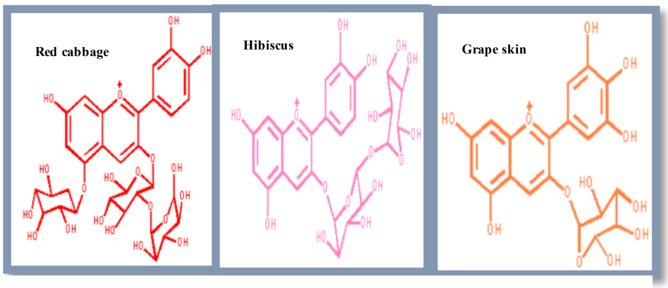


Fig 1. Molecular structures of anthocyanins

We used commercially available dyes extracted from red cabbage, hibiscus, and grape skin. First of all, cationic anthocyanins were purified by adsorption column XAD-7.[2] Then the purified dyes were dissolved in 5% aqueous formic acid and inserted into KF interlayers by the cation- exchange under stirring for 24 hours, followed by drying at 50°C. In every type of AN, we prepared a range of AN/KF samples to find the saturation point of the adsorbed anthocyanin between KF layers. The light durability of hybrid materials has also been investigated to evaluate differences in the color stability of anthocyanins.

With the difference in their molecular structures, specifically their sugar moieties, hybrid materials exhibited differences in saturated amounts of AN and interlayer distances. Our results showed that the color stability of AN/KF depends on the introduced amounts of AN. Moreover, the color stability of AN/KF from grape skin presented higher color stability over the saturation point. This was due to the small molecular volume and few number of sugar moieties on the AN from grape skin. Apart from the electrostatic interaction between AN and KF, the difference in sugar moieties caused the differences in properties of AN/KF which could be attributed to the self-association molecules of anthocyanin.

1) Kohno, Y., Hoshino, R., Matsushima, R., Tomita, Y., Kobayashi, K., 2007. Stabilization of flavylium dyes by incorporation in the clay interlayer. J. Jpn. Soc. Colour Mater. 80, 6–12.
2) Baublis, A., Spomer, A., Berber-Jimenez, M.D., 1994. Anthocyanin pigments: comparison of extract stability. J. Food Sci. 59, 1219–1221.

非溶媒誘起相分離法を用いた有機ー無機ハイブリッド多孔質膜の作製

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

Preparation of Organic-inorganic Hybrid Porous Membranes by Non-solvent Induced Phase Separation Method

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

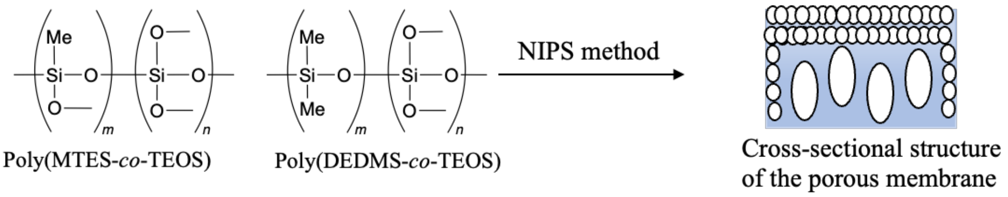
Silica membranes, as typified by inorganic separation membranes, have heat resistance and mechanical strength, and are expected to be applied to water treatment and gas separation. However, the current silica membranes are costly and heavy, and their use is limited due to the complexity of their preparation method. In this study, organic-inorganic hybrid membranes were fabricated by a simple non-solvent induced phase separation (NIPS) method1) using inorganic polysiloxane. NIPS method can form porous membranes by generating phase separation when a polymer dissolved in a good solvent is immersed in a non-solvent.

Poly(MTES-*co*-TEOS) and poly(DEDMS-*co*-TEOS) were prepared by sol-gel method with molecular weights of 91,000 and 130,000, respectively. When poly(MTES-*co*-TEOS) was dissolved in DMF at 70 wt% and deposited by a NIPS method, porous pores were observed. Poly(DEDMS-*co*-TEOS) membrane were non-porous because of the loose network derived from DEDMS monomer.

Keywords: Non-solvent induced phase separation method, Separation membrane, Siloxane.

シリカ膜に代表される無機分離膜は耐熱性や機械的強度を有し、水処理やガス分離への応用が期待される。しかし現状のシリカ膜はその成膜方法が煩雑であるため、高コスト・高重量であり、その利用範囲は限定的である。そこで本研究では、無機高分子であるポリシロキサンを用いて非溶媒誘起相分離法で成膜することで有機－無機ハイブリッド膜を作製した。非溶媒誘起相分離法は良溶媒に溶解させたポリマーを非溶媒に浸漬させることで相分離を発生させ、多孔質膜を成膜する方法であり、簡便な成膜が期待される。

アルコキシシランの加水分解・重縮合により poly(MTES-*co*-TEOS)及び poly(DEDMS-*co*-TEOS)をそれぞれ重量平均分子量 91,000 及び 130,000 で調製した。poly(MTES-*co*-TEOS)の 70wt%ジメチルホルムアミド溶液を用いて非溶媒誘起相分離法で成膜したところ、多孔質な孔が観察された。一方、poly(DEDMS-*co*-TEOS)から作製した膜の孔は緻密であった。これは 2 官能性モノマーである DEDMS に由来するネットワークの緩さによって孔がふさがったことが原因だと考えられる。



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1) D-M. Wang, J-Y. Lai, *Curr. Opin. Chem. Eng.*, **2**, 229-237 (2013).

POSS デンドリマーをフィラーとした有機－無機ハイブリッド膜の水分離特性

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

Water separation properties of organic- inorganic hybrid membranes using POSS dendrimers as fillers

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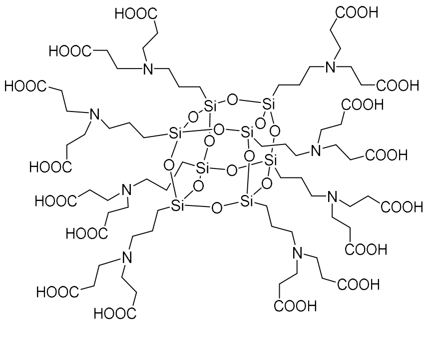
Reverse osmosis (RO) membranes are used in a wide range of fields, including seawater desalination. The aim of this study is to improve the water permeation performance by pore enlargement and increasing hydrophilicity. The synthesis of POSS dendrimers and the investigation of the properties of RO membranes were carried out.

POSS-COOH dendrimers were synthesized in three steps from 3-aminopropyl(triethoxy)silane in a total yield of 6.2%. NMR showed that the structure was stable in water for approximately 24 hours. DTA showed the decomposition temperature as 126 °C. Furthermore, the solubility of POSS-COOH to water was 18.9 wt%. We made an RO membrane using this POSS by an interfacial polymerisation method and conducted a water permeation test. The permeating velocity and salt rejection of the permeated water were measured. Water permeation tests show a salt rejection rate of 99 %, which is comparable to aromatic polyamide membranes. This is thought to be due to the repulsion between the carboxylate and chloride ions.

Keywords: Organic-inorganic Hybrid; Reverse Osmosis membrane; Polyhedral Oligomeric Silsesquioxanes



POSS-COOH Dendrimer

逆浸透(RO)膜は、海水淡水化など幅広い分野で使用されている。本研究の目的は、細孔の拡大と親水性の向上により、水の透過性能を向上させることである。そこで、POSS デンドリマーを合成し、その RO 膜の特性を検討した。

POSS-COOH デンドリマーは 3-アミノプロピル(トリエトキシ)シランから 3 段階で合成した [1]。NMR による追跡の結果、この構造は水中で約 24 時間安定であることがわかった。DTA により、化合物の分解温度は 126℃であった。さらに、POSS-COOH の水への溶解度は 18.9wt%であった。この POSS-COOH デンドリマーの水溶液を支持膜に注ぎ、上澄みを除去し、続いて BTESPA のヘキサン溶液を注ぎ、上澄みを除去し、加熱することで RO 膜を作成した。これを用いて水の透過試験を行い、水透過速度と塩阻止率を測定した。その結果、芳香族ポリアミド膜に匹敵する 99%の塩阻止率を示すことがわかった。これはカルボキシレートと塩化物イオンの反発によるものと考えられる。

1) K. Naka, M. Fujita, K. Tanaka, Y. Chujo, *Langmuir*, **2007**, *23*, 9057-9063.

水酸基を有するかご型シロキサンを添加した有機-無機ハイブリッド逆浸透膜の調製と評価

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

Preparation and evaluation of organic-inorganic hybrid reverse osmosis membranes with hydroxyl cage siloxane

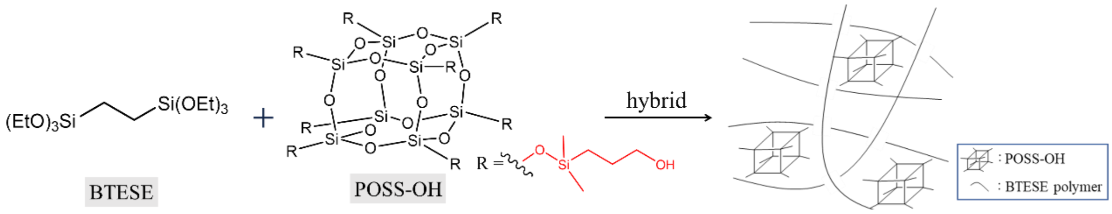
([1]*Faculty of Science and Technology, Tokyo University of Science*) ○ Rika Nagai,[1] Kazuki Yamamoto,[1] Takehiro Gunji[1]

Reverse osmosis (RO) membranes have an average pore size of less than 1 nm and are widely used in water treatment processes such as ultrapure water production because they block ions (Na+, Cl-, etc.) and allow water molecules to pass through. Currently, organic polymers are mainly used, and while they have excellent water permeance, they are difficult to clean due to their low heat resistance and chlorine resistance. Organic-inorganic hybrid RO membranes using inorganic polymers exhibit heat resistance and chlorine resistance derived from silicon atoms, but their water permeance is about 1/10 that of organic membranes.[1] In this study, RO membranes containing POSS-OH with hydroxyl groups were prepared in the hope of improving permeate flow rate due to pore expansion derived from the bulky backbone of POSS and hydrophilicity derived from the hydroxyl group. In fact, the best permeability was observed when the amount of POSS-OH added was 1 wt%. The membrane performance decreased when the amount of POSS-OH added was 5 wt% and 10 wt%. This may be due to the formation of aggregates among POSS due to the increase in the amount of POSS added.

Keywords: Organic-inorganic hybrid; Reverse osmosis membranes; Cage siloxane

RO 膜は平均孔径が 1 nm 以下であり、イオン（Na$^+$や Cl$^-$など）を阻止し水分子を通すため、超純水製造などの水処理プロセスで普及している。現在は主に有機高分子が使われており、優れた透水性能を有する一方、耐熱性、耐塩素性塩素が低く洗浄が困難である 。無機高分子を利用した有機無機ハイブリッド逆浸透膜は、ケイ素原子由来の耐熱性、耐塩素性を示すが、透水性能が有機膜の約 1/10 であることが課題である[1)]。本研究では、POSS のかさ高い骨格に由来する細孔拡張と水酸基に由来する親水性による透過流速の向上を期待し、水酸基を有する POSS-OH を添加した逆浸透膜を調製した。

実際、POSS-OH 添加量が 1wt%の時に、最も優れた透水性を示した。また、POSS 添加量が 5wt%, 10wt%では、膜性能は低下した。これは、POSS 添加量増加により POSS 同士が凝集体を形成したことによるものと考えられる。



1) R. Xu, J. Wang, M. Kanezashi, T. Yoshioka, T. Tsuru, *Langmuir*, **27**, 13996– 13999 (2011).

チタンホスホネートクラスターの合成と光触媒性能の評価

(東京理科大学 1)〇木村裕紀 1、山本一樹 1、郡司天博 1

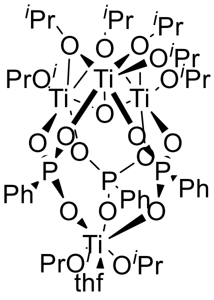
Synthesis of titanium phosphonate clusters and the evaluation of their photocatalytic performance (Tokyo University of Science1) ○Yuuki Kimura1, Kazuki Yamamoto1, Takahiro Gunji1

Titanium phosphonate clusters (TPCs) is a cage-shaped compound with phosphatitanoxane (Ti-O-P) bond. In our previous study, we reported that hydrolysates of TPC retaining the cage structure show a photocatalytic activity. This may be due to the fact that the cage structure of TPC resembles the rutile-type crystal arrangement of titanium dioxide in the upper part of the cage structure. Although the photocatalytic behavior of titanium dioxide is thought to be due to the myriad arrangements of Ti and O atoms, the limited atomic arrangement of TPC is presumed to be the photocatalytic factor as the smallest unit.

In this study, we report the photocatalytic redox properties of TPC, which was synthesized from titanium tetraisopropoxide and phenylphosphonic acid. 30 equivalents of YPV and its 2-propanol were dissolved in heavy toluene and the solution was irradiated with 365 nm UV light. The formation of acetone was traced by measuring 1H-NMR of the solution over time. The increase in acetone formation with increasing UV irradiation time indicated that TPC was reduced, and 2-propanol was oxidized, indicating that TPC has photooxidation-reduction properties.

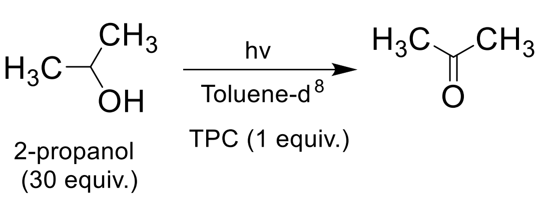
Keywords : Titanium phosphonate cluster, Titanium-oxo cluster, Photocatalyst, Organic-inorganic hybrid, Phosphatitanoxane bond

チタンホスホネートクラスター(TPC)はホスファチタノキサン(Ti-O-P)結合を有するカゴ型化合物である。我々はこれまでにカゴ構造を保持したTPCの加水分解物が光触媒活性を有することを報告した 1)。これはTPCのカゴ構造上部に酸化チタンのルチル型の結晶配列に類似していることに由来すると考えられる。酸化チタンが光触媒として振る舞うのはTi原子とO原子の無数の配列によるものであると考えられるが、TPCのもつ限られた原子配列が最小単位として光触媒の因子となっていると推定した。



TPC

そこで本研究ではTPCの光酸化還元性 2)を検討したので報告する。TPCはテトライソプロポキシドチタンとフェニルホスホン酸から合成した。YPVとその30当量の2-プロパノールを重トルエンに溶かし、その溶液に365 nmの紫外線を照射した。この溶液の ^{1}H-NMRを経時的に測定することによって、アセトンの生成を追跡した。紫外線の照射時間を増加するとアセトンの生成量が増加したことから、TPCが還元して2-プロパノールが酸化されたことがわかり、TPCが光酸化還元性を有することが分かった。



1) H. Tsukagoshi, Y. Sato, K. Yamamoto, R. Hayami, T. Gunji, *Appl Organomet Chem*, 2022. **36**, e6615.
2) T. Krämer, F. Tuna and S. D. Pike, *Chem, Sci*, 2019, **10**, e886-6898.

高フッ素化 POSS をフィラーとした新奇フッ素化高分子ハイブリッド材料の創出

（京大[1]・京大院工[2]）○國光 達明[1]・柴原 渓介[2]・権 正行[2]・田中 一生[2]

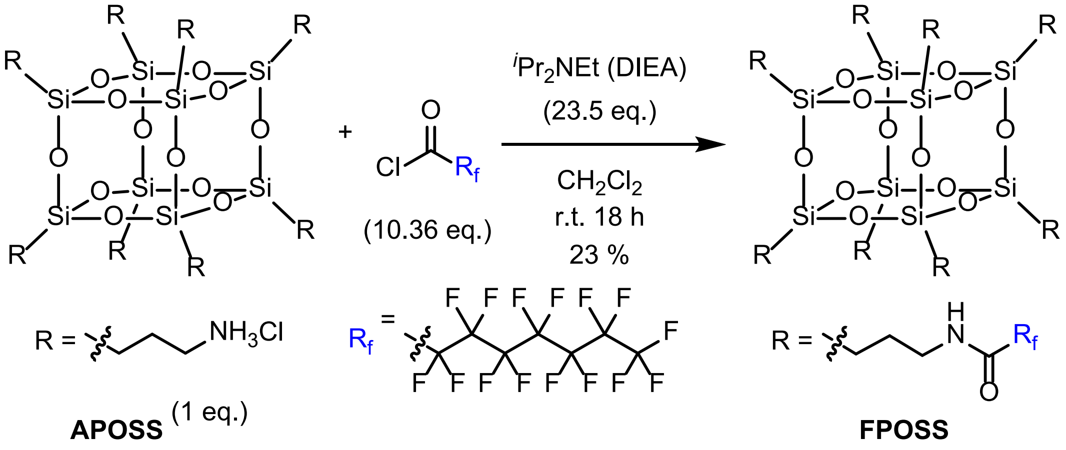
Development of Fluorinated Polymer Hybrid Materials with Highly Fluorinated POSS Fillers

([1]*Kyoto University*, [2]*Graduate School of Engineering, Kyoto University*) ○ Tatsuaki Kunimitsu,[1] Keisuke Shibahara,[2] Masayuki Gon,[2] Kazuo Tanaka[2]

Highly fluorinated polymers have many unique features such as a low refractive index, water and oil repellency, a low dielectric constant, and high chemical stability. However, they are insoluble in general-purpose organic solvents and do not mix well with other substances, which hinders the moldability of the materials and the possibility of precise control of physical properties using additives. We have recently reported that polyhedral oligomeric silsesquioxane (POSS) was highly valuable as a filler for polymer materials. [1] In this work, we synthesized a novel highly fluorinated POSS filler (**FPOSS**) (Scheme 1) and developed fluorinated polymer hybrid materials to further modify the properties of the fluorinated polymer. In this presentation, we will discuss the hybridization method and various properties of the hybrid materials.

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

高フッ素化ポリマーは低屈折率、撥水撥油性、低誘電率、高化学安定性など多数の特徴的な機能を有する一方で、汎用有機溶媒に溶けにくく、ほかの物質と混ざりにくいという性質は、材料の成型加工性や添加剤を用いた物性精密制御の可能性の妨げとなっていた。当研究室ではこれまでかご型シルセスキオキサン(POSS)が高分子材料のフィラーとしての利用価値が高いことを報告してきた[1]。本研究ではフッ素化ポリマーの性質を保ちつつさらなる物性改質を目的とし、新たに合成した高フッ素化POSS(**FPOSS**)をフィラーとしたフッ素化ポリマーハイブリッド材料の創出に取り組んだ(Scheme 1)。本発表では、ハイブリッド化の手法や各種物性について報告する。



Scheme 1. Synthesis of **FPOSS**.

1) Ueda, K.; Tanaka, K.; Chujo, Y. *Polymers* **2018**, *10*, 1332

Powderization of Gallium-Indium Eutectic Liquid Metal and Application to the Development of Functional Hybrids

(*Graduate School of Engineering, Kyoto University*) ○Christopher Hiromi Shimamura, Shunichiro Ito, Kazuo Tanaka

Keywords: Gallium-indium eutectic; Liquid metal; Composite materials; Stimulus response

Liquid metal is a general term for metals with melting points near room temperature and is a unique material that exhibits metal-derived properties such as high electrical conductivity while showing fluidity. Eutectic mixtures of gallium and indium (EGaIn), which are nontoxic and nonreactive, have attracted much attention in recent years as useful liquid metals and have been combined with polymer materials to create conductive films.[1] We have demonstrated that a low-molecular-weight alkyl thiol surfactant prevents EGaIn microdroplets from coalescence and enables us to handle them like a powder. The surfactant would modify the oxide layer or the exposed metal surface of the liquid metal droplets (Figure 1). The resulting *powderized* EGaIn (PLM) exhibits prominent properties like high hydrophobicity and ability to return to the *liquid bulk* from the powdery state when subjected to shear or compression (Figure 2). We developed a composite material of PLM and a silicone rubber that shows strain-induced enhancement of conductivity (Figure 3). Furthermore, it was demonstrated that the hydrophobic property of PLM enables us to fabricate a composite with a unique balloon-like shape (Figure 4). In the presentation, fabrication methods and properties of PLM and the resulting composite materials will be discussed in detail.

1) Zhou, X. *et al. J. Mater. Chem. A* **2021**, *9*, 10953–10965.

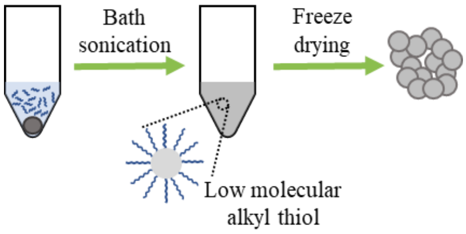


Figure 1. Preparation of PLM with an alkyl thiol surfactant.

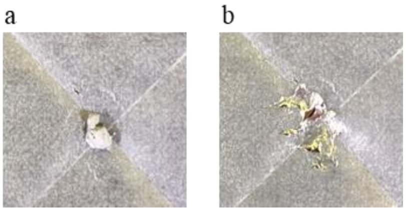


Figure 2. Photographic images of PLM (a) before and (b) after sheering.

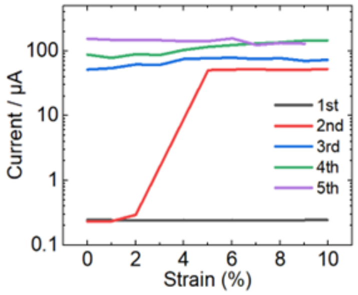


Figure 3. Strain-induced enhancement of electrical conductivity of LMP/silicone rubber composite.

Figure 4. Balloon-like shaped composite.

ポリアクリル酸を用いた有機架橋型ポリシルセスキオキサン系逆浸透膜の開発

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

Reverse osmosis membrane based on organic cross-linked polysilsesquioxane with polyacrylic acid

([1] *Faculty of Science and technology, Tokyo University of Science*) ○Masato Sugino,[1] Takahiro Gunji,[1] Kazuki Yamamoto [1]

Polysilsesquioxane-based reverse osmosis membranes have high chemical stability derived from siloxane bonds, and low water permeance performance. To increase hydrophilic properties of the membranes and water permeance, polyacrylic acid was introduced to the BTESPA reverse osmosis membranes. The water permeance of the BTESPA membrane with polyacrylic acid (M_w=5000) at the molar ratio of 2:1 increased more than three times compared to bare BTESPA membrane. Chemical cleaning of reverse osmosis membrane fouled by surfactants was also investigated. When the membrane was fouled by surfactant followed by cleaned by water and NaClO aqueous solution, the water permeance was restored to 76% compared to that of the initial performance.

Keywords：Reverse osmosis membrane; Silsesquioxane; Interfacial Polymerization; Fouling; Organic-inorganic Hybrids

海水の淡水化や超純水の製造に用いられる逆浸透膜は水分離膜の1つであり、芳香族ポリアミド膜が優れた水透過速度を示すことから広く用いられている。しかし、この逆浸透膜はファウリングに対して有効とされている塩素系薬品によって劣化する [1)]という欠点が指摘されている。本研究では、シロキサン結合由来の高い化学安定性を示すポリシルセスキオキサン系逆浸透膜について、水透過速度を改善するため、ポリアクリル酸を添加した膜を作製した。BTESPA 有機層、ポリアクリル酸(M_w=5000)を水層側に添加した場合、添加なしの膜と比べて水透過速度が最大 3 倍以上増加した。また、界面活性剤による逆浸透膜のファウリングに対しての次亜塩素酸ナトリウム水溶液を用いた洗浄効果についても評価したところ、界面活性剤によって目詰まりすることで水透過速度が初期性能の 45%まで低下し、続いて水と次亜塩素酸ナトリウム水溶液により洗浄することで 76%まで回復した。

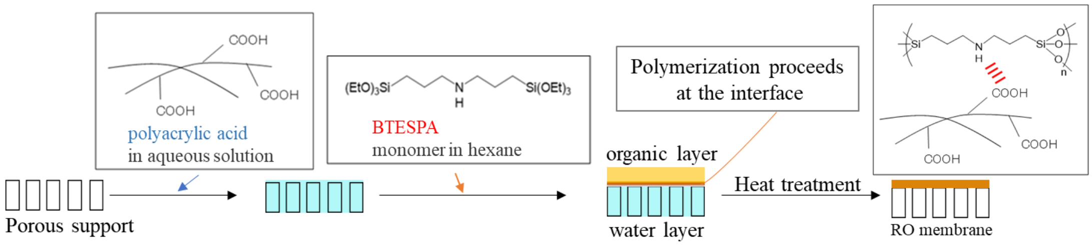


Fig. 1 Preparation of reverse osmosis membranes by interfacial polymerization

1) K. Yamamoto, S. Koge, S. Sasahara, T. Mizumo, Y. Kaneko, M. Kanezashi, T. Tsuru, J. Ohshita, *Bull. Chem. Soc. Jpn.*, 90, 1035-1040 (2017)

機械学習を活用したペロブスカイト薄膜の安定性評価

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Stability evaluation of perovskite thin films by machine learning

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Perovskite solar cells (PSCs) are attracting attention because of their low production cost and expecting high energy efficiency. On the other hand, they are susceptible to degradation by heat, water, and light, and their stability remains an issue. So, the development of batteries that excel in both efficiency and stability is required. The performance of PSCs varies greatly depending on the deposition process conditions, even when the same materials are used. Therefore, it is important to consider not only composition but also the process conditions to develop PSCs with higher performance. In this study, we compared the correspondence between the stability of devices considered in the data-driven way and the stability of perovskite thin films by experiments.

Keywords : Perovskite Solar Cells; Process informatics; Stability; Machine learning; Model interpretation

ペロブスカイト太陽電池は、製造コストが低く、高いエネルギー効率を実現しうることから注目されている。一方、熱・水・光により劣化しやすく、その安定性には課題が残るため、効率・安定性ともに優れたデバイスの開発が要求される。一般にペロブスカイト太陽電池の性能は、材料組成が同じでも成膜プロセス条件によって大きく異なる。そのため、より高性能な太陽電池の開発には、材料組成に加えプロセス条件も考慮した薄膜化・デバイス化が重要である。そこで本研究では、ペロブスカイト太陽電池の安定性を高める材料・プロセスを検討するため、機械学習によるデバイスの安定性解釈と、実験によるペロブスカイト薄膜の安定性を調べた。

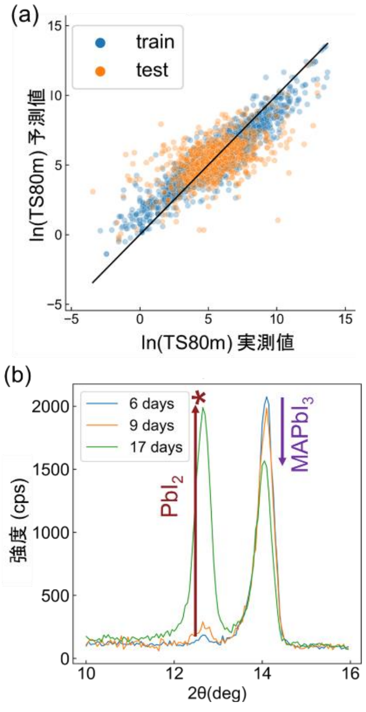

図 1. (a) 太陽電池の安定性回帰 (b) 40 分加熱した $MAPbI_3$ 薄膜の XRD ピークの時間変化

オープンデータベース [1]を用い、規格化した安定性指標 ln(TS80m)[2]に対する機械学習回帰を実施した(図 1a)。モデルの特徴量重要度を分析した結果、特にペロブスカイト層成膜中の溶媒や加熱処理時間・温度が、デバイス安定性に影響するプロセスだと分かった。そこで、成膜条件のうち加熱時間を振って $MAPbI_3$ ペロブスカイト薄膜を作製した。XRD 結果から劣化挙動を薄膜間で比較したところ、いずれも保存中に分解物 PbI_2 が増加し、そのうち最も長時間加熱したサンプルで PbI_2 が最も増加した(図 1b)。

1) T. J. Jacobsson, *et al.*, *Nat. Energy,* **2022**, *7*, 107-115.　2) Z. Zhang, *et al.*, *Nat. Comm.*, **2022**, 13, 7639.