Academic Program [Oral A] | 06. Analytical Chemistry：Oral A

Tue. Mar 19, 2024 9:00 AM - 11:40 AM JST | Tue. Mar 19, 2024 12:00 AM - 2:40 AM UTC
A1453(1453, Bldg. 14 [5F])

[A1453-2am] 06. Analytical Chemistry

Chair: Hideaki Yoshimura, Takahito Ohshiro

Japanese
9:00 AM - 9:10 AM JST | 12:00 AM - 12:10 AM UTC
[A1453-2am-01]
"Development of a Single-Molecule Identification Method for cGMP for understanding a Second messenger molecules"

○Kaho Fukuda[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2] (1. Kinransenri High School , 2. Osaka University, SANKEN)

English
9:10 AM - 9:20 AM JST | 12:10 AM - 12:20 AM UTC
[A1453-2am-02]
Development of a Single-Molecule Identification Method for Hydroxymethylcytosine in Tumor Marker Molecules

○Misaki Nakamura[1,2], Takahito Ohshiro[2], Komoto Yuki[2], Masateru Taniguchi[2] (1. Baika High School, 2. Osaka University, SANKEN)

Japanese
9:20 AM - 9:30 AM JST | 12:20 AM - 12:30 AM UTC
[A1453-2am-03]
Development of a Single-Molecule Detection Method for Acetylated Lysine in Gene Expression Regulation

○Yuno Notsu[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2] (1. Hyogo Prefectural Kakogawa Higashi High School, 2. Osaka University, SANKEN)

Japanese
9:30 AM - 9:40 AM JST | 12:30 AM - 12:40 AM UTC
[A1453-2am-04]
Development of a Single-Molecule Identification Method for Methyllysine Towards Elucidating and Diagnosing Muscular Dystrophy

○Ririna Hamasaki[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguti[2] (1. Osaka Ohtani High School, 2. Osaka University, ISIR)

Japanese
9:40 AM - 9:50 AM JST | 12:40 AM - 12:50 AM UTC
[A1453-2am-05]
Single-molecule study of acetylene dehydrogenation on Cu(111) surface

○Shoma Tateda[1,2], Minhui Lee[1,2], Maki Inagaki[2], Daiki Katsube[2], Emiko Kazuma[1,2], Yousoo Kim[1,2] (1. The Univ. of Tokyo, 2. RIKEN)

Japanese
9:50 AM - 10:00 AM JST | 12:50 AM - 1:00 AM UTC
[A1453-2am-06]

Real-space observation of CO_2 adsorption on silver surface using a scanning tunneling microscope

○Toru Okai[1,2], Minhui Lee[1,2], Maki Inagaki[2], Emiko Kazuma[1,2], Yousoo Kim[1,2] (1. The Univ. of Tokyo, 2. RIKEN)

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[A1453-2am-07]

Time Course Analysis of Oxidative Deterioration Gas from Structural Triacylglycerol Evaluated by HS-GCMS

○Hirofumi Sato[1], Kotaro Hattori[2], Atsushi Ohtaka[2] (1. ORIST, 2. Osaka Institute of Technology)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[A1453-2am-08]

Development of gas sensor system for early detection of cable fires

○Motomasa Sugitani[1], Wataru Tanaka[1], Takuro Hosomi[1], Tsunaki Takahashi[1], Jiangyang Liu[1], Takeshi Yanagida[1,2] (1. The Univ. of Tokyo, 2. Kyushu Univ.)

10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC

Break

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[A1453-2am-09]

Safety evaluation of Flame Retardants in polypropylene by dermal exposure

○Hiroto Idate[1], Maho Ishida[2], Masahiro Tokumura[2], Tomohiro Shirai[1], Takanori Miyazaki[1], Masakazu Makino[2] (1. Tosoh Corporation, 2. University of Shizuoka)

English
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[A1453-2am-10]

Robust SnO_2 Nanofilm Gas Sensor with Sb Dopant and Metal Nanoparticle Catalysts under Environmental Variation

○XI WANG[1], Haruka Honda[1], Tsunaki Takahashi[1], Chaiyanut Jirayupat[1,3], Wataru Tanaka[1], Takuro Hosomi[1], Chia-Hsiu Chen[3], Mitsuru Irie[3], Takeshi Yanagida[1,2] (1. Graduate School of Engineering, The University of Tokyo, 2. Graduate School of Engineering Sciences, Kyushu University, 3. MI-6.Ltd, Tensho Office Nihonbashi, 8-13 Kobunecho, Nihonbashi, Chuo-ku, Tokyo)

English
10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
[A1453-2am-11]

Interfacial engineering and structure control for highly sensitive nanocellulose quartz crystal microbalance humidity sensor

○JING ZENG[1], Wataru Tanaka[1], Takuro Hosomi[1], Tsunaki Takahashi[1], Jiangyang Liu[1], Takeshi Yanagida[1,2] (1. Graduate School of Engineering, The University of Tokyo, 2. Graduate School of Engineering Sciences, Kyushu University)

Japanese
11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC
[A1453-2am-12]

A Simple Method for Measuring Butyrylcholinesterase by Optode

○Ryo Sato[1], Takashi Masadome[1] (1. Shibaura Institute of Technology)

English
11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC
[A1453-2am-13]

Development of Paper-based Analytical Device for Nucleic Acid Quantification Combining CRISPR/Cas12a System and Personal Glucose Meter

○Yohei Tanifuji[1], Guodong Tong[1], Yuki Hiruta[1], Daniel Citterio[1] (1. Keio University)

Japanese
11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC
[A1453-2am-14]

Concentration Measurement of Urea using Quartz-Based Single-Mode Optical Waveguides

○Takumi Usukura[1], Sato Naoki[1], Matsubara Noritaka[1] (1. Furukawa electric co.ltd)

Japanese
11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC
[A1453-2am-15]

Evaluation of amount of Candida mannan in a saliva by plasmon-enhanced fluorescence imaging

○Ryuto Noumi[1], Masaya Yako[1], Yasunori Nawa[1], Keiko Tawa[1], Hiroshi Kurita[2] (1. Graduate school of science and technology, Kwansei Gakuin Univ, 2. Department of Dentistry and Oral Surgery, Graduate School of Medicine, Shinshu Univ.)

情報伝達物質のサイクリックグアニン分子の１分子識別法の開発

（金蘭千里高等学校 [1]，大阪大学 [2]）○福田佳帆 [1]，大城 敬人 [2]、小本 祐貴 [2]、谷口 正輝 [2]
Development of a Single-Molecule Identification Method for cGMP for understanding a Second messenger molecules ([1]Kinransenri High School, [2] *Osaka University*) ○ Kaho Fukuda[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2]

Cyclic guanosine monophosphate (cGMP), a second messenger, is involved in many physiological processes such as neurotransmission, vascular regulation, cell proliferation, plasticity, and cardiac function, and requires precise regulation. is important. In this study, we conducted high-speed current measurements of cyclic guanosine (cGMP) and its control molecule GMP using nanogap electrodes, and performed machine learning by extracting features from the signals. As a result, we achieved high discrimination ability from similar substances such as cAMP and GMP. Since cGMP is associated with a variety of diseases, this technology will contribute to the advancement of future medical research.
Keywords：Single-Molecule Detection; Nucleotide; Epigenetic modification; Nano-device

情報伝達物質であるサイクリックグアノシン一リン酸(cGMP)は、生物機能を考えるうえで、神経伝達、血管調節、細胞増殖、可塑性、心臓機能など、多くの生理学的プロセスに関与し、正確な調整が重要である。そもそも cGMP は，体内では細胞内のエネルギー伝達やシグナル伝達に使われるグアノシン三リン酸（GTP）から生成され、さらに cGMP は加水分解され GMP に分解される（図 1）.

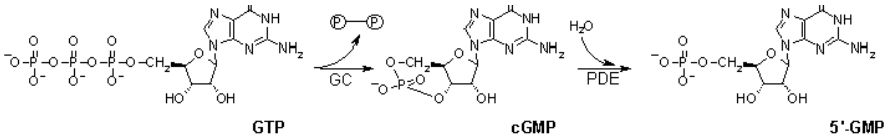


図 1　cGMP の合成、分解スキーム

本研究では、サイクリックグアノシン(cGMP)の１分子識別を目的とする．これまで，当研究室では核酸塩基などの生体分子の１分子識別に成功している [1)-4)]．　cGMP の識別では，その類似分子である GMP や GTP，cAMP との識別が必要となる．測定溶液として、cGMP および類似分子である GTP や GMP，cAMP の水溶液を濃度 1μM に調製しこれを用いた．この溶液を１分子ごとの電気伝導度を，ナノギャップ電極により高速電流計測を行った．その結果、１分子ごとの電流シグナルを得ることに成功した．このシグナルから特徴量を抽出し，機械学習による１分子の識別を試みた。その結果，類似物質と F1 値 0.7 以上の識別を達成した．このことから，cGMP の１分子識別により，生体内での情報伝達の理解をすすめることにつながると考えられる．

引用: 1) *Sci. Rep.* **2021**, *11*, 19304, 2) Sci.Rep., **2019**, 9, 3886，3）*Nat. Nanotech.* **2014**, 9,835-840 4) *J. Phys. Chem. C*, 2019, 123, 15867−15873

Development of a Single-Molecule Identification Method for Hydroxymethyl Cytosine in Tumor Marker Molecules

([1]*Baika High School,* [2] *Osaka University, ISIR*) ○Misaki Nakamura[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2]

Keywords: DNA, RNA, Single-Molecule Detection, Tunnel-Current, Epigentics

Cancer is the most common cause of death in Japan, and it is said that one in two people will develop cancer at some point in their lifetime [1)]. Early diagnosis can reduce the burden of treatment and lower the mortality rate [2)]. Therefore, there is a demand for fast and accurate diagnostic methods. Hydroxymethyl cytidine (5-hmC: See Figure) is gaining attention as an epigenetic marker for cancer. 5-hmC can be detected before symptoms appear, enabling early detection. Conventional detection methods include mass spectrometry and conversion of modified nucleic acids (5-hmC) to different nucleobases followed by sequencing.

In this study, we focused on hydroxymethyl cytidine (5-hmC), an oxidized modification of cytosine in DNA and RNA, and employed single-molecule quantum measurement for the detection of this modified molecule (5-hmC). This method has the advantage of directly detecting and identifying molecules in an aqueous solution on a single-molecule basis. So far, we have successfully identified single molecules of nucleobases and amino acids using highly sensitive and rapid electrical measurement technology with a nano-gap electrode device [3)-6)]. For the measurement solution, we adjusted the concentration to 1uM using 5-hmC and cytidine (C), a control molecule. We conducted rapid current measurements with the nano-gap electrode. As a result, we successfully obtained current signals for each molecule. From these signals, we extracted characteristic features and attempted to identify single molecules through machine learning. As a result, we successfully created a classifier with an F-measure value of over 0.8 for distinguishing between 5-hmC and C. This technology is expected to be applied to early diagnosis and prognostic evaluation of cancer.

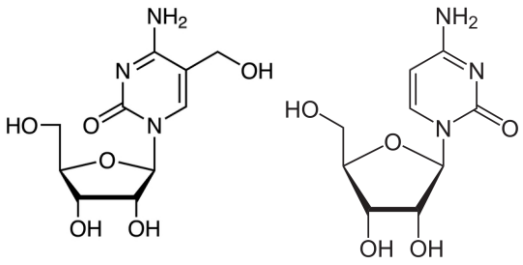


Figure:(Left) Hydroxymethyl Cytidine (5-hmC), (Right): Cytidine

Reference: 1). 国立がん研究センターがん情報サービス (https://ganjoho.jp/reg_stat/statistics/stat/summary.html) 2). 国立がん研究センター https://www.ncc.go.jp/jp/information/pr_release/2020/0317/ncc_press_release_20200317_01.pdf. 3) *Sci. Rep.* 2021, 11, 19304, 4) *Sci.Rep.*, 2019, 9, 3886, 5) *Nat. Nanotech.* 2014, 9,835-840 6) *J. Phys. Chem. C*, 2019, 123, 15867−15873

遺伝子発現制御にかかわるアセチル化リジンの１分子検出法の開発

(兵庫県立加古川東高等学校[1]、 大阪大学[2]) ○野津柚乃[1]、大城 敬人[2]、小本 祐貴[2]、谷口 正輝[2]

Development of a Single-Molecule Detection Method for Acetylated Lysine in Gene Expression Regulation ([1]Hyogo Prefectural East Kakogawa High School, [2] Osaka University, ISIR) ○Yuno, Notsu[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2]

This study developed a method to identify and measure acetylated lysine, a crucial marker in histone acetylation, at the single-molecule level. Detecting acetylated lysine is vital for understanding gene expression control mechanisms through quantifying histone acetylation. Using a nano-gap electrode, we measured both acetylated and unmodified lysine molecules. Machine learning analysis of the measured signals revealed high discriminative ability. Future detection of acetylated lysine in histones is expected to enable quantitative visualization of gene expression.
Keywords : Single-Molecule Detection; Nucleotide; Epigenetic modification; Nano-device

タンパク質のエピジェネティクス研究は、細胞の発生、成長、疾患の発症における重要なプロセスを理解に繋がり、将来的に疾患の治療や予防に役立つ可能性がある重要な分野である。これまでタンパク質のアミノ酸修飾として、アセチル化とメチル化などが報告されており、アセチル化は主に転写活性化に寄与し、メチル化は遺伝子発現の調節と染色体の安定性に関与することが知られている。

本研究では、遺伝子発現の制御理解に不可欠であるヒストン中のリジンのアセチル化に注目し、アセチル化リジンの一分子レベル識別・計測法の開発を試みた。ナノギャップ電極を用いて、アセチル化リジンと未修飾リジン分子の高速電気計測技術を行った．これまでに、ナノギャップ電極デバイスによる高速電気計測技術を利用し、核酸塩基・アミノ酸などの生体分子の１分子識別に成功している[1)-4)]。実験はまず、測定溶液として、アセチル化リジン および対照分子であるリジンの水溶液を濃度 1μM に調製し、これを用いた。ナノギャップ電極を用いてこの溶液の高速電流計測を行った。その結果、１分子ごとの電流シグナルを得ることに成功した。このシグナルから特徴量を抽出し、機械学習による１分子の識別を試みた。その後，アセチル化リジンとリジンの 1 分子シグナルのデータの 80%をもちいて分類器を学習させ、残りのテスト用データを識別し精度を評価した。その結果、精度 0.8 以上の分類器の作成に成功した。本研究は、ヒストンのアセチル化リジン検出を通じた遺伝子発現の定量的可視化が期待される。

引用: 1) Sci. Rep. 2021, 11, 19304, 2) Sci.Rep., 2019, 9, 3886，3）Nat. Nanotech. 2014, 9,835-840 4) J. Phys. Chem. C, 2019, 123, 15867−15873

筋ジストロフィー症解明・診断に向けたメチルリジン１分子識別法の開発

（大阪大谷高等学校[1], 阪大[2]）○濵﨑鈴和[1]，大城 敬人[2]、小本 祐貴[2]、谷口 正輝[2]
Development of a Single-Molecule Identification Method for Methyllysine Towards Elucidating and Diagnosing Muscular Dystrophy ([1]Osaka Ohtani High School, [2]Osaka University, ISIR) ○ Ririna Hamasaki[1], Takahito Ohshiro[2], Yuki Komoto[2], Masateru Taniguchi[2]

This study developed a method to identify and measure methylation modifications of lysine related to muscular dystrophy. Utilizing a nano-gap electrode device for high-sensitivity, rapid electrical measurements, methylated lysine molecules were identified at the single-molecule level. The data obtained were analyzed using machine learning, with the discriminative ability assessed based on the F-value. The results confirmed a high capability in distinguishing differences in methylation and the presence or absence of methylation. This method holds promise for applications in diagnosing muscular dystrophy, understanding its pathology, and developing treatments.
Keywords : RNA; Single-Molecule Detection; Tunnel-Current; Epigentics

筋肉が弱くなる老化現象や, 若年で筋肉が徐々に弱くなる筋ジストロフィーという疾患がある．この原因の一つとして，筋肉のミオシン中に存在するアミノ酸であるリジンの後天的修飾が，筋力低下に関係していることが報告されている．本研究では筋ジストロフィーに関連するリジンのメチル修飾に注目し，この修飾検出法として 1 分子検出法を用いることとした。これまで，ナノギャップ電極デバイスによる高感度・高速の電気計測技術を利用し、核酸塩基・アミノ酸などの生体分子の１分子識別に成功している [1)-4)].

本研究では、メチルリジン モノメチル体：1Mlys1Mlys，ジメチル体:2Mlys，トリメチル体：3 Mlys の１分子識別を目的とする． メチルリジンの識別では，その類似分子であるリジンとの識別が必要となる．測定溶液として、メチルリジン（1Mlys，3 MlysMlys）および類似分子であるリジンの水溶液を濃度 1 μ M に調製し，これを用いた．この溶液を，ナノギャップ電極により高速電流計測を行った．その結果、１分子ごとの電流シグナルを得ることに成功した. このシグナルから特徴量を抽出し，機械学習による 1 分子の識別を試みた。その結果，類似物質リジンでと各メチル化リジンとの識別能が F 値としては 0 5 以上とする学習器を作成することに成功した．ここでは，メチル化リジン分子を一分子レベルで識別を目的とする機械学習による F 値評価で高い識別能を得られたことから、メチル化の有無や程度の差異を明確に検出できることを示唆している。この技術は筋ジストロフィーの診断、病態理解、治療法開発に応用が期待される。

引用: 1) Sci. Rep. 2021, 11, 19304, 2) Sci.Rep., 2019, 9, 3886，3）Nat. Nanotech. 2014, 9,835-840, 4) J. Phys. Chem. C, 2019, 123, 15867−15873

Cu(111)表面におけるアセチレンの脱水素化反応に関する単一分子レベル研究

（東大[1]・理研[2]）○舘田 匠馬[1,2]・李 民喜[1,2]・稲垣 万貴[2]・勝部 大樹[2]・数間恵弥子[1,2]・金 有洙[1,2]

Single-molecule study of acetylene dehydrogenation on Cu(111) surface ([1]*The Univ of Tokyo*, [2]*RIKEN*) ○Shoma Tateda[1,2], Minhui Lee[1,2], Maki Inagaki[2], Daiki Katsube[2], Emiko Kazuma[1,2], Yousoo Kim[1,2]

Acetylene is used as a carbon source in the synthesis of graphene[1] and silicon carbide[2] by chemical vapor deposition. For these syntheses using acetylene, a dehydrogenation reaction occurs on the surface as the first step of the reaction. In this study, we deposited acetylene on Cu(111) single crystalline surface and investigated the dehydrogenation reaction of a single acetylene molecule by scanning tunneling microscopy (STM). The combination of the STM analysis and density functional theory calculation allows us to elucidate the process of the dehydrogenation reaction. When the tunneling current was applied at the bias of 3.0 V from the STM tip above a single acetylene molecule, the dehydrogenation reaction was observed (Fig. 1). The current trace measurements show that the two hydrogen atoms dissociated at one step or almost simultaneously (Fig. 2).

Keywords : Surface Reaction; Single-molecule study; Dehydrogenation; Scanning Tunneling Microscope; Density Functional Theory

アセチレンは化学気相成長法によるグラフェン[1]や炭化ケイ素[2]の合成において炭素源として利用される。これらの合成では、反応の第一段階として表面における脱水素化が進行すると考えられる。本研究は、表面におけるアセチレンの脱水素化過程を単一分子レベルで明らかにすることを目的とし、Cu(111)単結晶表面に吸着したアセチレン単一分子の脱水素反応を走査トンネル顕微鏡（STM）により観測した。STMによる反応の解析と密度汎関数理論を用いた計算を比較することで、単一分子の脱水素反応の反応過程を解明した。アセチレン単一分子の上に STM 探針を配置し+3.0 V の電圧を印加すると、分子の反応が観察された（Fig. 1）。また、トンネル電流の変化から、2 つの水素がほぼ同時に解離していることが明らかとなった（Fig. 2）。

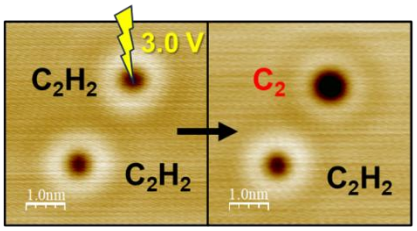


Fig.1 Dehydrogenation reaction of acetylene induced with tunneling current.

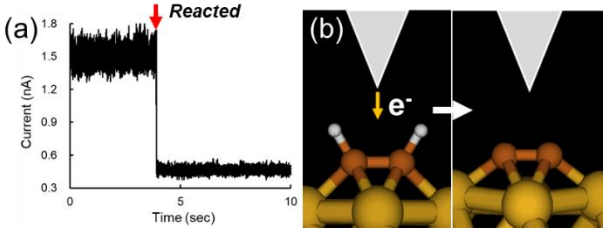


Fig.2 (a) Current trace measurement. (b) Schematic illustration of dehydrogenation reaction with STM tip.

[1] H. Ago *et al.*, *Appl. Phys. Express* **2013**, 6, 075101. [2] C. F. Wang and D. S. Tsai, *Mater. Chem. Phys.* **2000**, 63, 196.

本研究は環境省「地域資源循環を通じた脱炭素化に向けた革新的触媒技術の開発・実証事業」の支援の下で実施された。

日本化学会 第104春季年会 (2024)

走査トンネル顕微鏡を用いた銀表面上における CO_2 の吸着状態の実空間観測

(東大[1]・理研[2]) ○小粥 徹[1,2]・李 民喜[1,2]・稲垣 万貴[2]・数間 恵弥子[1,2]・金 有洙[1,2]
Real-space observation of CO_2 adsorption on silver surface using a scanning tunneling microscope (*[1]The Univ. of Tokyo [2]RIKEN*) ○Toru Okai[1,2], Minhui Lee[1,2], Maki Inagaki[2], Emiko Kazuma[1,2], Yousoo Kim[1,2]

Recently, many studies have been conducted on CO_2 reduction using metal catalysts. Most studies have been based on macroscopic analysis and microscopic analysis of interaction between metal surfaces and CO_2 molecules is not sufficiently performed. In this study, we focused on the adsorption process which is the first step of metal-catalyzed reactions. We conducted microscopic analyses of the adsorption structure of CO_2 molecules on Ag(110) using a scanning tunneling microscope at a molecular level. We found that CO_2 molecules formed islands on Ag(110) (Fig 1), with unit cells composed of two different states of molecules (P and L). To further investigate the interactions between the surface and molecules, we applied a voltage pulse on a single molecule of P and L. The molecule under the tip was desorbed at a negative voltage (Fig 2). We found the desorption energies of P and L are different, which indicates that the degree of surface-molecule interactions is different for P and L.
Keywords : CO_2, Adsorption structure, Analysis of single molecule, Scanning tunneling microscope

近年、金属触媒を用いた CO_2 還元反応の研究が盛んに行われている。既往研究の多くは巨視的な分析に留まり、金属表面と CO_2 分子の微視的な相互作用に関する分析が不足している。本研究では金属触媒反応における複数の素過程の中で、第一段階である吸着過程に着目し、分子分解能を持つ走査トンネル顕微鏡を用いて Ag(110) 上に吸着した CO_2 分子を実空間観測し、分子の吸着状態の微視的な分析を行なった。

CO_2 分子は Ag(110) 表面上において島を形成し(Fig 1)、島は二つの異なる吸着状態の分子(P、L)からなる単位格子を持つことがわかった。さらに分子と基板の相互作用について分析するため、P、L 分子それぞれの直上に探針から電圧を印可し、その前後での形態変化を観測すると、探針直下の分子の脱離現象が確認された(Fig 2)。しかし脱離する電圧の閾値には違いが見られた。この脱離エネルギーの違いは、P と L で分子と基板の間に存在する相互作用が異なることによって生じたと考えられる。

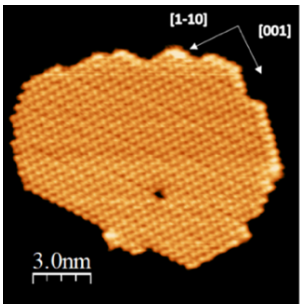


Fig 1. CO_2 island on Ag(110). (V = 20 mV、I = 100 pA)

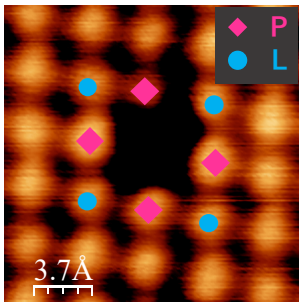


Fig 2. Desorption of L species under the tip. (V = 20 mV、I = 100 pA)

HS-GCMS 分析による構造トリアシルグリセロールの酸化劣化ガスの経時変化

((地独)大阪産業技術研究所 [1]・大阪工業大学 [2]) ○佐藤 博文 [1]・服部 幸太朗 [2]・大高 敦 [2]

Time Course Analysis of Oxidative Deterioration Gas from Structural Triacylglycerol Evaluated by HS-GCMS ([1]*Osaka Research Institute of Industrial Science and Technology*, [2]*Osaka Institute of Technology*) ○Hirofumi Sato,[1] Kotaro Hattori,[2] Atsushi Ohtaka[2]

Triacylglycerol (TAG), a major component of edible lipids, is degraded by various factors to produce deterioration gaseous compouds such as aldehydes and carboxylic acids. Previous studies have shown that radicals around the double bond are generated and the methylene double bond is peroxidized, from which various alkyl aldehydes are formed. In our study, we observed the aldehydes generated from structural lipids, such as triolein, as substrates over time, and observed the formation of shorter chain aldehydes that did not conform to the known cleavage pattern. Therefore, when we observed degradation behavior using nonanal as a substrate, we found that formates and alcohols were formed, suggesting that a Beyer-Villiger-type carbon reducing reaction was taking place (Figure 1).

Keywords : Lipid oxidation; Oxidative degradation, Deterioration gaseous compounds; Head space gas chromatography

食用脂質の主成分であるトリアシルグリセロール (TAG) は種々の要因で劣化してアルデヒドやカルボン酸などの劣化ガスを生じる。これまでの研究で二重結合周辺にラジカルが発生し、二重結合メチレン周辺がペルオキシド化され、ここから種々のアルキルアルデヒドが生成することが知られている。我々の研究では、構造脂質、たとえばトリオレインを基質にして発生するアルデヒドを経時的に観測したところ、時間とともに既知の開裂パターンに合致しない短鎖アルデヒドの生成も確認された。そこで、ノナナールを基質に劣化挙動を観察したところ、ギ酸エステルやアルコールが生成していることがわかり、バイヤービリガー型の減炭素反応が起きていることが示唆された (図 1)。

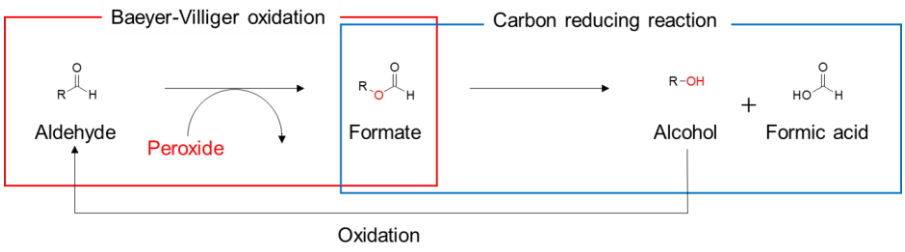


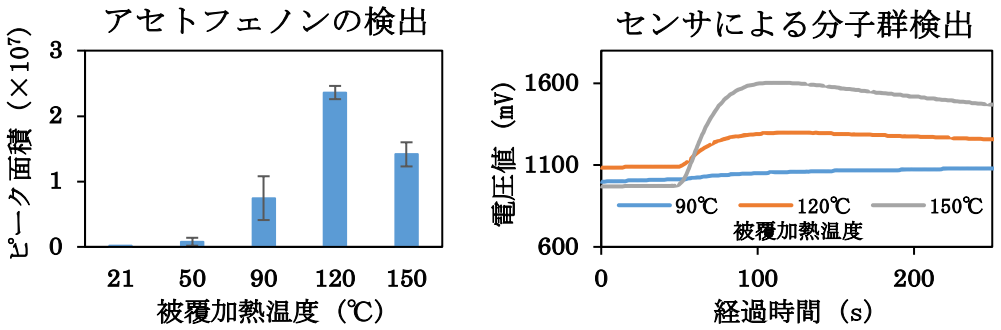
図 1 減炭素反応の予想メカニズム

ケーブル火災の早期検出に向けたガスセンサーシステムの開発

（東大院工 [1]・九大先導研 [2]）○杉谷 元優 [1]・田中 航 [1]・細見 拓郎 [1]・高橋 綱己 [1]・Jiangyang Liu[1]・柳田 剛 [1,2]
Development of gas sensor system for early detection of cable fires ([1]*Graduate School of Engineering, Tokyo University*, [2]*Institute for Materials Chemistry and Engineering, Kyushu University*) ○Motomasa Sugitani,[1] Wataru Tanaka,[1] Takuro Hosomi,[1] Tunaki Takahashi,[1] Jiangyang Liu,[1] Takeshi Yanagida[1,2]

Electrical fires are most common fires in factories and workspaces. One of the main causes of electrical fires is abnormal overheating of electrical cables. For early detection of the overheating, infrared cameras are practically used to monitor the temperature of electrical cables. However, infrared cameras cannot detect the temperature of crowded electrical cables. In this study, we aim to construct a semiconductor gas sensor system that can detect odor molecules released from the insulation films and the sheaths as the temperature of electrical cables rise. A 600 V vinyl insulated wire (IV wire) was heated and the released gas were analyzed by gas chromatography mass spectrometry. We detected several volatile organic molecules released at temperatures higher than the conventional working temperature and lower than the melting temperature of the IV wire. In addition, we successfully detected these molecules by two commercially available semiconductor gas sensors.
Keywords : Cable fires; Early detection; Semiconductor gas sensor; Gas chromatography mass spectrometry

電気火災は、工場・作業所における火災で最も大きな割合を占める。電気火災の主な原因の 1 つに、電気ケーブルの過熱異常があげられる。過熱異常の早期発見に向けて、赤外線カメラを用いた電気ケーブルの温度をリアルタイムモニタリングするシステムが実用化されているが、混み合った配線の温度検知が困難という課題がある。本研究では、電気ケーブル火災を未然に防ぐために、電気ケーブルの温度上昇に伴い絶縁被膜・シースから放出される匂い分子を検出可能な半導体ガスセンサシステムの構築を目的とする。600V ビニル絶縁電線(IV 線)の絶縁被膜・シースを加熱して、ガスクロマトグラフィー質量分析を行ったところ、正常温度より高温かつ溶融温度より低温でアセトフェノンなど複数の分子が放出されることが分かった(左図)。また、市販の 2 種類の半導体ガスセンサによって、これらの分子群の検出に成功した(右図)。



ポリプロピレンに含まれる難燃剤の経皮曝露試験を通じた安全性評価

（東ソー株式会社[1]・静岡県立大[2]）○井立 寛人[1]・石田 真穂[2]・徳村 雅弘[2]・白井 智大[1]・宮崎 高則[1]・牧野 正和[2]
Safety evaluation of Flame Retardants in polypropylene by dermal exposure ([1]*Tosoh Corporation*, [2]*University of Shizuoka*) ○Hiroto Idate,[1] Maho Ishida,[2] Masahiro Tokumura,[2] Tomohiro Shirai,[1] Takanori Miyazaki,[1] Masakazu Makino[2]

Flame retardants (FRs) are indispensable chemicals to our safe and affluent lives, which are used to improve the fire resistance performance of materials such as plastics and fibers. On the other hand, there are concerns about the adverse effects of some FRs on the human body and the environment, and the safety evaluation of FRs has attracted much attention in recent years. In this study, we evaluated the safety of polypropylene resin containing brominated flame retardants (BFRs) by a dermal exposure test using an artificial skin model. The results indicated that skin absorption of BFRs with relatively large molecular weight and high lipophilicity (Log K_{ow} = 6.6~13.0) was below the detection limit. On the other hand, BFRs with low molecular weight and moderate lipophilicity (Log K_{ow} = 4.5) exhibited skin permeability. In the presentation, we will also report the result of a similar dermal exposure test on polymeric BFRs.
Keywords : Flame Retardants; Dermal Exposure; Safety Evaluation

難燃剤はプラスチックや繊維などの可燃性を低下させる添加剤であり、我々の豊かな生活に欠かせない化学物質である。一方、難燃剤の中にはヒトや生態系に害を及ぼす可能性があり、その安全性評価は近年ますます重要となっている[1, 2]。

本研究では、臭素系難燃剤を含むポリプロピレン樹脂と人工皮膚モデルを使用した経皮曝露試験にて、難燃剤種と樹脂劣化状態が皮膚吸収に与える影響を解析した。その結果、比較的に分子量が大きく親油性が高い（logK_{ow}=6.6～13.0）難燃剤の皮膚透過量は検出限界以下であった。一方で、低分子量かつ適度な親油性を有する（logK_{ow}=4.5）難燃剤は皮膚吸収を認めた。また、高分子型の臭素系難燃剤に関して同様の経皮曝露試験を実施したので、併せて報告する。

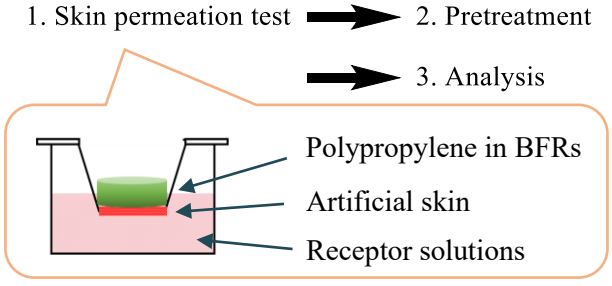


Fig. 1 Procedure of skin permeation measurement of BFRs

Table. 1 Skin permeation test results

BFRs	MW	log K_{ow}	Skin Permeation (ng / mL)
A	778	4.5	530
B	951	6.6	<20
C	1067	13.0	<20
D	943	13.0	<20

1) Liu, X. et al. *Chemosphere* **2017**, *168*, 272.
2) Abdallah, M. A.; Harrad, S. *Environ. Int.* **2018**, *118*, 26.

Robust SnO_2 Nanofilm Gas Sensor with Sb Dopant and Metal Nanoparticle Catalysts under Environmental Variation

([1]*The Univ. Tokyo,* [2]*MI-6 Ltd.,* [3]*Kyushu Univ.*) ○ Xi Wang,[1] Haruka Honda,[1] Tsunaki Takahashi,[1] Chaiyanut Jirayupat,[1,2] Wataru Tanaka,[1] Takuro Hosomi,[1] Chia-Hsiu Chen,[2] Mitsuru Irie,[2] and Takeshi Yanagida[1,3]

Keywords: Gas Sensor; Metal Oxide Semiconductor; Robustness; Metal Catalyst; Doping

Environmental fluctuations, particularly in ambient humidity, can impact the metal oxide gas sensors' responses. In this study, we propose a strategic approach to mitigate the effects of environmental variability on the responses of metal oxide semiconductor gas sensors through the utilization of a heavily doped metal oxide nanofilm channel (2 wt% antimony-doped tin oxide: ATO) and metal catalyst nanoparticles.

Although the sensor response of ATO channels to ethylene decreased significantly compared to that of non-doped SnO_2 channels, the change in sensor response under humidity variation was much less than that of SnO_2 (Fig. 1). XPS analysis indicate that the amount of oxygen on the ATO surface is smaller than that on non-doped SnO_2, indicating reduced redox reactions between gas molecules and surface oxygen (Fig. 2). In addition, the Sb doping could have a masking effect on the changes in sensor electrical resistance due to undesired redox reactions because the number of Sb-induced carriers is much larger than defect-induced carriers (e.g., oxygen vacancies) which are affected by redox reactions.[1] Therefore, ATO is considered to be a robust sensor channel with low activity in redox reactions. Furthermore, Pt nanoparticle modification of ATO surface significantly improves the sensor response with reduced variation of sensor response under humidity fluctuations. This may be due to the electrical and catalytic effects of the Pt particles on ATO surface.[2] As a result, the LOD values were lowest for the sensor with Pt particles modified on ATO.

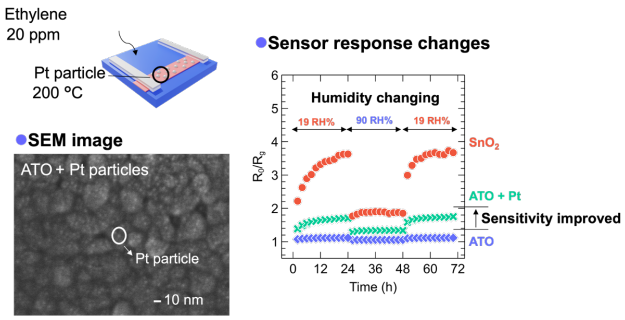


Fig. 1 SEM image and ATO with Pt nanoparticles sensor response during humidity variation.

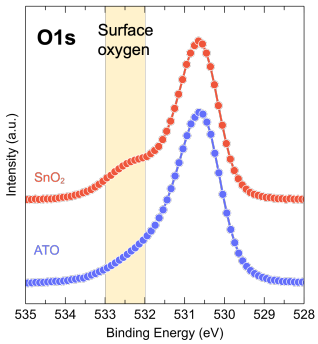


Fig. 2 O1s XPS spectra of SnO_2 and ATO

1) *Sensors and Actuators: B. Chemical.* **2022**, 371, 132603.
2) C. Jiang, *Angew. Chem. Int. Ed.* **2013**, 52, 6265.

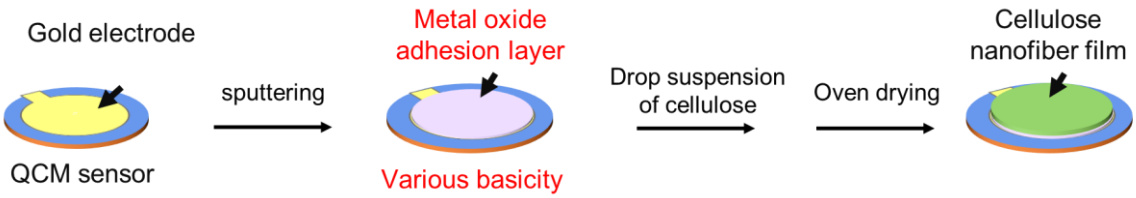
Interfacial engineering and structure control for highly sensitive nanocellulose quartz crystal microbalance humidity sensor

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Graduate School of Engineering Science, Kyushu University*) ○ Jing Zeng,[1] Wataru Tanaka,[1] Takuro Hosomi,[1] Tsunaki Takahashi,[1] Jiangyang Liu,[1] Takeshi Yanagida[1,2]

Keywords: Humidity sensor; Cellulose; Metal oxide; Adhesive layer

Cellulose, a highly hydrophilic, abundant, and renewable bioresource, is emerging as an effective humidity sensing material. Cellulose coated on Quartz crystal microbalance (QCM) as humidity sensor is attracting scientific attention recently. Many researchers have modified functional group of cellulose as well as combined cellulose with polymer or carbon materials to further increase the sensing performance of cellulose coated QCM sensors. But few research has studied the interfacial effect between the electrode and the sensing layer. Because of the insufficient adhesive strength between the cellulose and the Au electrode of QCM, a robust adhesive layer is worthy of investigation to enhance the stability and sensitivity of the sensors.

Herein, a Quartz crystal microbalance (QCM) sensor coated with metal oxide thin film and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-oxidized cellulose which contains abundant carboxy acid groups has been fabricated as a humidity sensor by simple dropping and oven drying method. Four types of metal oxide species are fabricated at Au electrode of QCM sensor via radio frequency sputtering as interfacial layer, including Nickel Oxide (NiO), Zinc Oxide (ZnO), Titanium Oxide (TiO_2), Tungsten Trioxide (WO_3). The NiO interfacial layer shows better humidity sensitivity enhancement, owing to its higher basicity and hydrophobicity, leading to intensive bulk shape of dispersion solution, resulting in denser and thicker sensing film of cellulose on QCM. To study the enhancement mechanism, the bulk shape of sensing film, the hydrophilicity of metal oxides interfacial layer was studied.



オプトードによるブチリルコリンエステラーゼの簡易測定法の検討

○佐藤 怜[1], 正留 隆[1] (1. 芝浦工業大学)

A Simple Method for Measuring Butyrylcholinesterase by Optode

○Ryo Sato[1], Takashi Masadome[1] (1. Shibaura Institute of Technology)

Butyrylcholinesterase (BuChE) is produced in the liver, making it possible to quantify liver metabolic function through blood tests. The disadvantages of the conventional BuChE assay recommended by the Japanese Society for Clinical Chemistry (JSCC) are the use of expensive reagents and the need for expensive automated analyzers. In addition, there is a need for a rapid and simple BuChE assay that can screen emergency patients. μ-Paper Based Analytical Devices (μPADs) are chemical analysis systems in which a detection unit is placed on a piece of paper and a solution is permeated into the unit. The decrease in concentration of myristoylcholine chloride (MyrCh), a substrate of BuChE, is detected by an optode that responds to MyrCh. As a result, determination of BuChE is possible. In this study, we investigated a simple, inexpensive, and rapid detection method for BuChE using μPAD with an optode as a detector. A linear relationship between ΔE and BuChE concentration was obtained in the BuChE concentration range of 0-0.2 units-mL^{-1}.

Keywords : Optode, Enzymes, Simplified Analytical Method, μ-Paper Based Analytical Devices

ブチリルコリンエステラーゼ(BuChE)は肝臓で生成されることから，血液検査によって肝臓の代謝機能を数値化することが可能である. BuChE の従来の測定法である日本臨床化学会勧告法は，高価な試薬や，自動分析装置を用いることが欠点である．さらに，救急患者のスクリーニングが可能な BuChE の迅速，簡便な測定法も求められている． μ-Paper Based Analytical Devices (μPADs)は，紙上の感応部に試料溶液を浸透させることで，化学分析を実現するものである. BuChE の基質である塩化ミリストイルコリン(MyrCh) が分解されることによる MyrCh の濃度減少を MyrCh に応答するオプトードで検出することで, BuChE 濃度の間接的定量が可能となる．そこで，本研究では，この原理を利用して BuChE の μPADs オプトードによる簡便，安価，迅速な検出法を検討した．その結果, Fig. 1 に示すように, 0～0.2 units･mL^{-1} の濃度範囲の BuChE 水溶液に対して，感応部の色差(ΔE)と BuChE 濃度との間に直線関係が得られた.

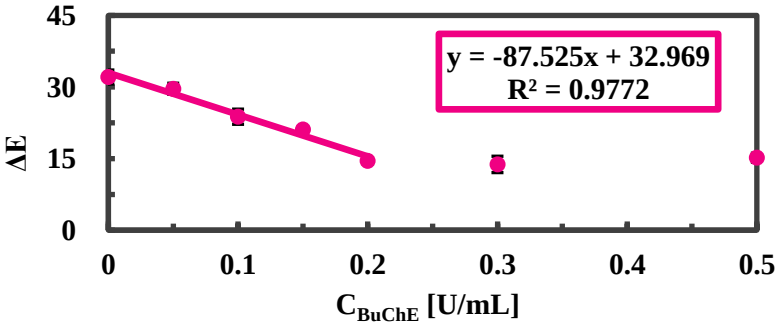


Fig. 1 BuChE に対する検量線

Paper-based Device for Point-of-care Nucleic Acid Quantification Using CRISPR/Cas System and Personal Glucose Meter

([1]*Graduate School of Science and Technology, Keio University*) ○Yohei Tanifuji,[1] Guodong Tong,[1] Yuki Hiruta,[1] Daniel Citterio[1]

Keywords: *DNA quantification; CRISPR/Cas; Paper-based device*

Recently, clustered regularly interspaced short palindromic repeat (CRISPR)-based assays have been reported as attractive tools for nucleic acid detection due to their high specificity and sensitivity. Taking advantage of the low cost and wide availability of personal glucose meters (PGMs), methods combining the CRISPR/Cas system and PGMs for nucleic acid quantification have been reported for point-of-care testing (POCT). They rely on the conversion of the target nucleic acid concentration into a glucose signal through an enzymatic reaction. However, most reported assays require multi-step operations involving pipetting and separation, which is against the concept of POCT.

In this work, we developed a paper-based biosensor for quantification of nucleic acids by combining the CRISPR/Cas system and PGMs. Pre-deposition of all required reagents on a multi-layer paper device enables assays to be performed by end-users without multiple operation steps and reagent handling. The device consists of three layers of hydrophobic wax-patterned paper (Fig. 1). A target DNA-specific Cas12a-CRISPR RNA (crRNA) complex and single-stranded DNA-conjugated invertase immobilized on magnetic beads (MB probe) are deposited on the first layer, while sucrose is dried on the third layer. Application of a sample containing target DNA (tgDNA) onto the first layer of the paper device activates the Cas12a-crRNA complex, resulting in release of invertase through nonspecific trans-cleavage of ssDNA at the surface of the MB probe. After the cleavage reaction, removing a hydrophobic film separating the first and second paper layers allows the released invertase to flow through the second filter layer, while magnetic beads are retained. When reaching the third layer, the released invertase converts the pre-deposited sucrose to glucose, which is subsequently detected by the PGM. A tgDNA concentration response was obtained from a single sample application (10 μL) without any further user intervention except for the hydrophobic film removal and washing buffer application (Fig. 2). For proof-of-concept, the detection of human papillomavirus-DNA (43 base pairs) has been achieved.

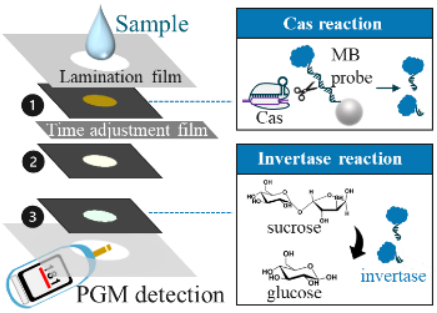


Fig. 1 Device design

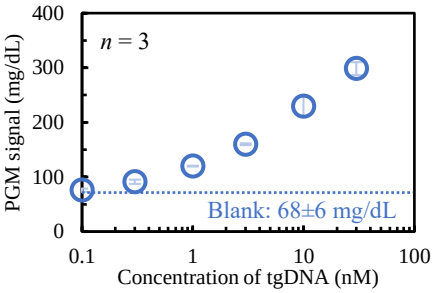


Fig. 2 Calibration curve with device

石英系シングルモード光導波路を用いた尿素濃度計測

（古河電工[1]）○臼倉 拓弥[1]・佐藤 直樹[1]・松原 礼高[1]
Urea Concentration of Measurement Using Silica-based Single-mode Optical Waveguides
([1]*FURUKAWA Electric co. ltd*) ○Takumi Usukura,[1] Naoki Sato,[1] Noritaka Matsubara[1]

The optical sensing technology is widely used in various fields such as industry, environment, and healthcare due to its resistance to electromagnetic noise. In this study, we investigated the feasibility of a sensor device based on a silica-based single-mode planar lightwave circuit (PLC) using the Attenuated Total Reflection (ATR) method. Silica is a material with transparency in the visible and near-infrared regions, as well as high chemical and heat resistance. Additionally, the single-mode PLC allows for precise control of waveguide and cladding thickness, enabling accurate adjustment of light absorption.

We developed an ATR-PLC device by monolithically integrating multiple single-mode waveguides with different optical path lengths on a single chip (Figure 1a). Near-infrared light (wavelength: 1400 nm) was introduced into the device, and the absorption intensity of the evanescent wave was measured by contacting the device surface with a urea solution. As a result, we observed a monotonic increase in the absorption intensity with respect to the ratio of optical path lengths, where the minimum path length was set to 1 (Figure 1b). We also obtained a correlation between the concentration of the urea solution and the absorption intensity. These results suggest the potential of ATR measurements using PLC as an optical sensor, and further details will be presented in the upcoming presentation.
Keywords : Silica-based optical waveguide; single mode; ATR; Urea;

光センシング技術は電磁ノイズに強く、工業、環境、医療などの幅広い分野で利用されている。本研究では、ATR（Attenuated Total Reflection）法を利用した石英系シングルモード光導波路(Planar Lightwave Circuit ： PLC)を用いて、エバネッセント波の光吸収によるセンサデバイスの検討を行った。石英は可視帯と近赤外帯で透明性があり、耐薬耐熱性も高い材料である。また、シングルモード光導波路は導波路やクラッド厚を微細に制御することで、光吸収量を高い精度で調整することができる。

光路長の異なる複数のシングルモード光導波路をワンチップにモノリシック集積したATR-PLCデバイスを作製した(図1a)。本デバイスに近赤外光(λ：波長1400nm)を入射させ、尿素水溶液をデバイス表面へ接触させて光吸収強度を測定した。その結果、最小光路長を1とした光路長の比に対して単調的な増加（図1b)を観測し相関が得られた。また尿素水溶液の濃度依存性についても光吸収強度を測定し相関が得られた。本結果はPLCを用いたATR測定が光センサとして利用できることを示唆しており、当日の発表にて詳細を報告する。

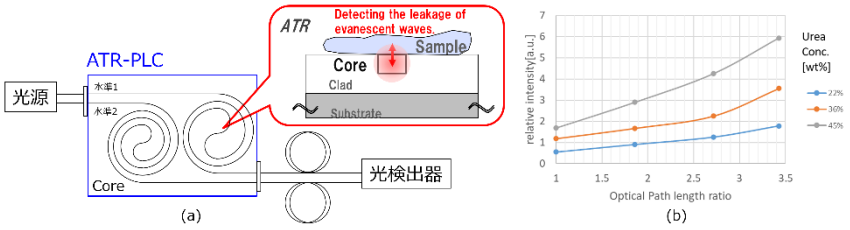


図 1. (a)ATR-PLC 概念図　(b) 相対光強度と光路長の関係

プラズモン増強イメージングによる唾液中のカンジダマンナン定量評価

(関西学院大院理工[1]・信州大医[2]) ○能見 隆登[1]・八子 将也[1]・名和 靖矩[1]・田和 圭子[1]・栗田 浩[2]

Evaluation of amount of *Candida* mannan in a saliva by plasmon-enhanced fluorescence imaging ([1]*Kwansei Gakuin Univ.*, [2]*Shinshu Univ.*) ○Ryuto Noumi[1], Masaya Yako[1], Yasunori Nawa[1], Keiko Tawa[1], Hiroshi Kurita[2]

Candida mannan contained in oral *Candida* serves as an immunity marker. Highly sensitive and rapid quantitative detection of *Candida* mannan can be used for health management. In our laboratory, *Candida* mannan has been detected using an angle-scanning type of surface plasmon-enhanced fluorescence spectroscopy and quantitatively evaluated in saliva. In this study, *Candida* mannan was detected in saliva using simple and rapid technique of fluorescence microscopy. A sandwich assay was constructed with capture antibody, *Candida* mannan extracted by heat treatment of saliva, detection antibody, and fluorescently labeled antibody. Fluorescence intensity in the *Candida* mannan assay was evaluated using an upright microscope with a Cy5 filter and a 4x objective lens. As a result, 9.7-fold fluorescence intensity was observed on the plasmonic pattern of a chip by analyzing fluorescence images. *Candida* mannan in saliva was detected at concentrations of 0.08 and 0.25 ng/ml.

Keywords : Candida Mannan; Saliva; Plasmon; Immunosensor; Microscope

口腔カンジダ菌に含まれるカンジダマンナンは、免疫力マーカーとしての役割を果たすことが栗田らによって示されてきた[1]。カンジダマンナンの高感度かつ迅速定量検出が可能になれば、この数値を基準にした健康管理ができる。これまで当研究室では、角度走査型表面プラズモン増強蛍光測定装置を用いてカンジダマンナンの検出を行い、唾液検体中のカンジダマンナンを 0.05～0.25 $ngml^{-1}$ の濃度範囲で定量的に評価できた[2]。本研究では、より簡便で迅速な評価ができる蛍光顕微鏡を用いた唾液検体中のカンジダマンナンの検出に取り組んだ。カンジダマンナン捕捉抗体をチップ表面に結合し、唾液の熱処理から得られたカンジダマンナン、カンジダマンナン検出抗体、Alexa647 標識二次検出抗体でサンドイッチアッセイを構築した。

蛍光観察では Cy5 フィルターと 4 倍の対物レンズを用いた。蛍光落射像の解析から、プラズモニックパターン上での蛍光増強度が 9.7 倍であることがわかった。また、唾液検体中のカンジダマンナンを濃度 0.08 ng/ml と 0.25 ng/ml で定量的な評価ができた(Fig.1)。

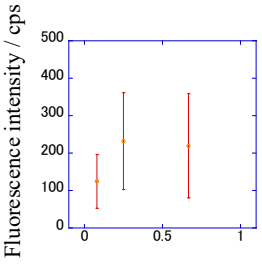


Fig.1 Fluoresce intensity plotted against the concentration of *Candida* mannan in saliva.

1) K. Hayashi, et al, *Journal of Oral and Maxillofacial Surgery, Medicine, and Pathology* **2017**, 29, 65.
2) M. Yako et al., *Jpn. J. Appl. Phys.* **2023**, 62, SG1028.