

Title of Project : Catalytic Bond-Cleavage Reactions toward Utilization of Renewable Resources

Kyoko Nozaki
(The University of Tokyo, Graduate School of Engineering,
Professor)

Research Project Number : 18H05259 Researcher Number : 60222197

Keyword : Renewable resources, Catalyst, Reduction, Bond-cleavage, Metal–ligand cooperative effect

【Purpose and Background of the Research】

The chemical industry has developed a method of converting exhaustible fossil resources into various useful substances. Synthetic chemistry is the major stream, that assembles simple constituents such as C2~5 fractions and BTX (benzene · toluene · xylenes) given by cracking naphtha obtained from petroleum. Also, most of the conventional chemical processes are oxidation of these highly reduced carbon compounds.

On the other hand, different methodology will be needed for utilization of biomass such as lignin and grease, which are renewable carbon resources. Since the carbon atoms in renewables are often highly oxidized, it is necessary to reduce the carbon atoms for the effective utilization of them. Furthermore, as renewable resources are often mixtures of complex compounds, "decomposition chemistry" need to be considered in order to convert the macromolecules into small molecules for easy handling.

This research aims to develop catalytic bond-cleavage reactions, which are necessary when considering effective use of renewable carbon resources.

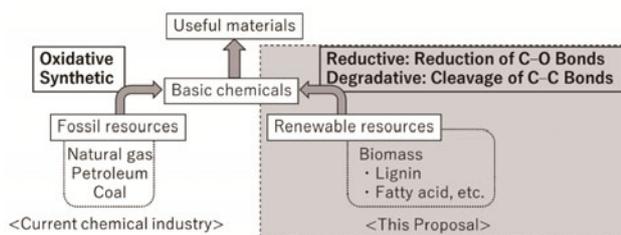


Figure 1. The purpose of this research.

【Research Methods】

1. Reductive cleavage of C–O bonds in the reduction of highly oxidized resources: Especially toward the synthesis of aromatic hydrocarbons and their analogues from lignin, we aim to develop selective hydrogenolysis catalyst of C–O bond in phenol and aryl methyl ether which are commonly found in the partial structure of lignin.

2. Cleavage of C–C bonds contributing to decomposition of complex structures: Toward utilization of aliphatic carboxylic acids, we focus on

the decarboxylation–dehydrogenation of aliphatic carboxylic acids. The dehydrogenation–decarbonylation from aliphatic alcohols and aldehydes will be also examined. In addition, the dehydrogenation–retro-aldol reaction of a 1,3-diol structure, a partial structure of lignin, will be also investigated. These findings will pave the avenue of basic science toward the production of basic chemicals from renewable resources.

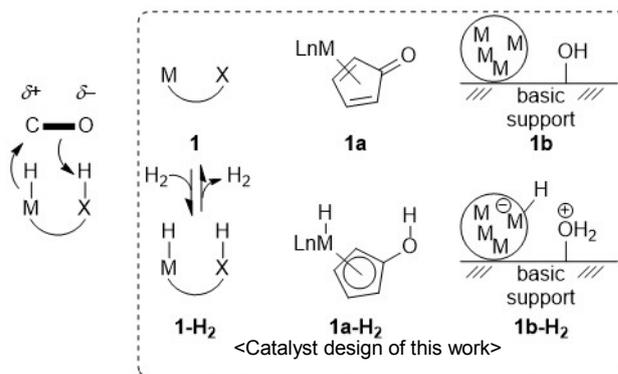


Figure 2. Approach of this study.

【Expected Research Achievements and Scientific Significance】

The concept of catalytic design in homogeneous catalysis will be expanded to heterogeneous systems. The success of this research opens up a new field of "decomposition chemistry".

【Publications Relevant to the Project】

- Direct and Selective Hydrogenolysis of Arenols and Aryl Methyl Ethers. S. Kusumoto, K. Nozaki *Nat. Commun.*, **2015**, *6*, 6296.
- The Retro-Hydroformylation Reaction. S. Kusumoto, T. Tatsuki, K. Nozaki *Angew. Chem. Int. Ed.* **2015**, *54*, 8458.

【Term of Project】 FY2018-2022

【Budget Allocation】 147,900 Thousand Yen

【Homepage Address and Other Contact Information】

<http://park.itc.u-tokyo.ac.jp/nozakilab/indexE.html>



Title of Project : Multiscale Interfacial Molecular Science for Innovative Functional Materials

Takuzo Aida
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Professor)

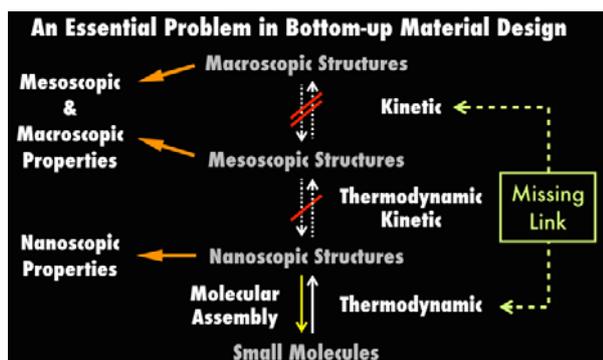
Research Project Number : 18H05260 Researcher Number : 00167769

Keyword : Supramolecular Chemistry, Hybrid Materials, Physical Perturbations, Surface/Interface

【Purpose and Background of the Research】

A remarkable progress in supramolecular chemistry in the last two decades now allows us to design and tailor a variety of desired nanostructures by optimizing a thermodynamic control. However, there still remains an essential missing link between molecular/nano structures and those with meso/macroscopic size regimes. This is mainly because the assembling events from “nanoscale size regimes” toward “upper hierarchical levels” suffer from an irreversible interference by numerous kinetic traps, leading to the formation of ill-defined macroscopic structures. On the other hand, in living system, many biological events rely on certain macroscopic structural anisotropies of biomaterials. Those anisotropic structures are constructed under physical perturbations such as electrical potentials, ion/fluid fluxes, osmotic pressures, and shear forces.

Having a lesson from biological assembling events, we are taking up the challenge of filling the above-mentioned “missing link” by applying physical perturbations to our highly reputed assembled motifs.



【Research Methods】

In this project, we will mainly focus attention on utilization of three chemical motifs (1)–(3), all of which require a certain structural anisotropy up to a macroscopic length scale for their practical applications. Motif (1) is the first self-repairable polymer glass. Motif (2) is ionic liquid-based polyelectrolites showing extra-large capacitance. Motif (3) is a non-spherical polyelectrolyte such as titanate nanosheets with

orientation properties in a magnetic field.

【Expected Research Achievements and Scientific Significance】

This project will cause a big paradigm shift in industrial technologies as well as basic sciences. (1) Development of self-repairing polymer glass is important for application to various types of self-repairing plastics, leading to a major step toward achieving sustainable development goals (SDGs). (2) Large capacitance of polyelectrolytes leads to practical applications as large-capacity electricity storage devices. (3) Anomalous behaviors of non-spherical polyelectrolytes are utilized for the development of “anisotropic colloid science”, which will open up a new field of material science and will pave the way for a full-fledged artificial muscles and cartilages. We apply a variety of physical perturbations to control kinetic events of the assembly of large-dimension nanostructures and achieve structural anisotropies.

【Publications Relevant to the Project】

- Y. Yanagisawa *et al.* Mechanically robust, readily repairable polymers via tailored noncovalent cross-linking, *Science* **359**, 72–76 (2018).
- M. Matsumoto *et al.* Ultrahigh-throughput exfoliation of graphite into pristine ‘single-layer’ graphene using microwaves and molecularly engineered ionic liquids, *Nature Chem.* **7**, 730–736 (2015).
- M. Liu *et al.* An anisotropic hydrogel with electrostatic repulsion between cofacially aligned nanosheets, *Nature* **517**, 68–72 (2015).

【Term of Project】 FY2018-2022

【Budget Allocation】 148,800 Thousand Yen

【Homepage Address and Other Contact Information】

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Title of Project : Chemistry of Boron-Containing π -Electron Materials

Shigehiro Yamaguchi
(Nagoya University, Institute of Transformative Bio-Molecules,
Professor)

Research Project Number : 18H05261 Researcher Number : 60260618

Keyword : boron, p-electron system, planarization, supramolecular polymer, radical

【Purpose and Background of the Research】

Introduction of boron atoms into π -conjugated skeleton produces π -electron materials with characteristic electronic structures. In particular, group 13 boron can impart electron-accepting character to a π -skeleton due to an empty p-orbital of boron. For instance, triphenylborane is isoelectronic with triphenylmethyl cation and doping of boron atoms into graphene imparts semiconducting properties. In general, however, boron-containing materials are unstable due to high Lewis acidity. Steric protection of the boron center is necessary for gaining sufficient stability.

With regard to this issue, we recently found that structural constraint in a planar fashion enables producing stable boron-containing π -electron systems despite the absence of steric protection. Based on this design principle, we have so far synthesized a series of planarized boron-containing π -electron materials and investigate their characteristic properties. This chemistry can be regarded as a model study of boron-doped graphenes. Beyond this perspective, herein we aim at producing unusual properties and functions by making best use of characteristic features of planarized boron π -skeleton (Fig. 1).

【Research Methods】

Planarization of triarylboranes gives rise to 1) electron-accepting properties through effective orbital interaction between the empty p-orbital of boron and π -skeleton, 2) high Lewis acidity due to the absence of steric congestion, and 3) π -stacking ability due to the planar structure. Exploiting these features, we will pursue unusual photophysical and electronic properties and achieve controlling the self-assembled structure through the formation of supramolecular polymers. For instance, we recently developed a boron-stabilized π -radicals, which showed ambipolar carrier transporting ability in single crystal FET. We will tackle on more unusual and superb radical materials based on this type of π -skeletons. Moreover, we will synthesize various types of attractive planar π -electron materials and supramolecular polymers.

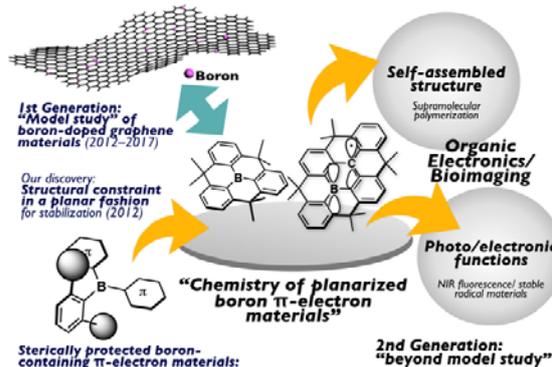


Fig. 1 Chemistry of planarized boron-containing π -electron materials

【Expected Research Achievements and Scientific Significance】

Understanding and exploitation of determinant factors of elements that govern materials functions are a fundamental issue of chemistry. Our approach in this project would contribute to progress not only in organoboron or main-group chemistry, but also in materials science, particularly organic electronics. Application to bioimaging would be also an important direction of this chemistry.

【Publications Relevant to the Project】

- T. Kushida, S. Shirai, N. Ando, T. Okamoto, H. Ishii, H. Matsui, M. Yamagishi, T. Uemura, J. Tsurumi, S. Watanabe, J. Takeya, S. Yamaguchi, *J. Am. Chem. Soc.*, **139**, 14336-14339 (2017).
- Z. Zhou, A. Wakamiya, T. Kushida, S. Yamaguchi, *J. Am. Chem. Soc.*, **134**, 4529-4532 (2012).

【Term of Project】 FY2018-2022

【Budget Allocation】 149,000 Thousand Yen

【Homepage Address and Other Contact Information】

<http://orgreact.chem.nagoya-u.ac.jp/olddocs/Home.html>



Title of Project : Chemistry of Adaptable Space

Susumu Kitagawa
(Kyoto University, Institute for Advanced Study, Institute for Integrated Cell-Material Sciences, Distinguished Professor)

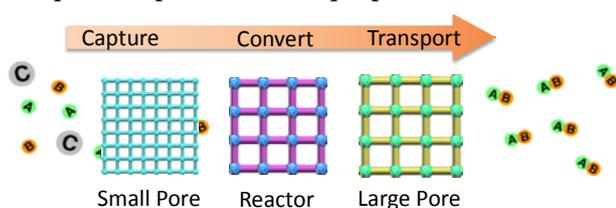
Research Project Number : 18H05262 Researcher Number : 20140303

Keyword : Porous Coordination Polymer, Dynamic Function, Interface, Mass Transportation

【Purpose and Background of the Research】

Living organisms adapt themselves to various environmental changes. From chemistry standpoint, this spontaneous adaptation function is realized by the establishment of a “flow” that governs nano-level multiple functions such as transmitting molecular signals and transferring ions between inside and outside the cell membrane. In this research, we design a basic operation of living organisms such as reception, detection, transfer, conversion, etc. into porous materials by encoding those functional essences in dynamic nanospaces, to establish a new scientific paradigm of porous materials that respond to various environmental changes and signals.

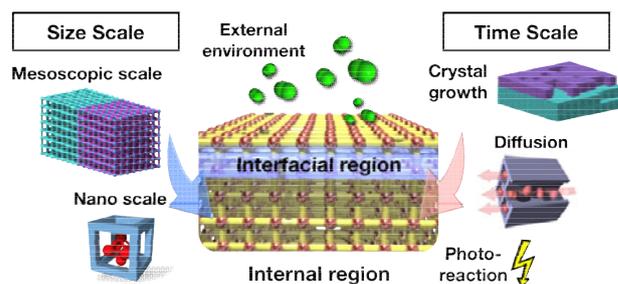
Specifically, Porous Coordination Polymers (PCP, Metal–Organic Framework: MOF) is mainly used as a nanospace platform for developing targeted functions. Chemistry for fusing different PCP crystals will be studied and developed to establish fundamental technologies for creating flows that amplify and propagate molecular signals. This represents the system and theory in “Chemistry of Adaptable Space” that we propose.



【Research Methods】

An important issue in creating the adaptive space is the development of an organic fusion method of PCP crystals. Designs of crystallite size, electric charge and molecular motions in nanopores as well as understanding interface structures of PCP crystals are essential foundation of this research.

For the fusion of PCP crystals and nanopore domains, we apply epitaxial growth method¹ and synthesis of molten PCP² that we have developed. Synthesis of asymmetric PCP single crystals having different pore diameters and static potentials, etc., will be targeted to realize the flow that propagates and transmits stimuli and signals.



【Expected Research Achievements and Scientific Significance】

Following outcomes are anticipated: (1) Development of new materials that separate, capture and convert in response to concentrations of component gas species such as CO₂, CO, CH₄, O₂, etc. in exhaust gas, flue gas, and biogas, etc. (2) Applications to such as membranes that regulate ionic species such as Li⁺, Na⁺, Ca²⁺, and NH₄⁺, etc. and spontaneously control their conductivity in response to external environment. This research will lead to the creation of materials with synergistic molecule/information conversion function which cannot be obtained by individual function of a single substance.

【Publications Relevant to the Project】

- 1.“Sequential Functionalization of Porous Coordination Polymer Crystals.” Hirai, K.; Furukawa, S.; Kondo, M.; Uehara, H.; Sakata, O.; Kitagawa, S. *Angew. Chem. Int. Edit.* **2011**, *50*, 8057–8061.
- 2.“Reversible Solid-to-Liquid Phase Transition of Coordination Polymer Crystals” Umeyama, D.; Horike, S.; Inukai, M.; Itakura, T.; Kitagawa, S. *J. Am. Chem. Soc.*, **2015**, *137*, 864–870.

【Term of Project】 FY2018-2022

【Budget Allocation】 149,500 Thousand Yen

【Homepage Address and Other Contact Information】

<http://www.kitagawa.icems.kyoto-u.ac.jp>



Title of Project : Creative Research and Development of Incoherent Nonlinear Photoswitchable Molecules

Jiro Abe
(Aoyama Gakuin University, College of Science and Engineering,
Professor)

Research Project Number : 18H05263 Researcher Number : 70211703

Keyword : Photochromism, Photochemistry, Nonlinear Optical response

【Purpose and Background of the Research】

Photochromic molecules, which can reversibly interconvert between stable and metastable isomers upon exposure to light, are key elements for the development of photo-responsive systems that offer promising perspectives in the materials and life sciences. However, traditional photochromic molecules require the use of high-energy UV light for isomerizing in at least one direction. The use of UV light comes with inherent limitations for a range of applications that arise from irreversible chemical damage and limited penetration depth in many materials. Moreover, background light causes an undesired photochromic reaction because a linear absorption of light would occur even for one photon irradiation.

Recently, we have developed novel fast photochromic molecules which involve the stepwise two-photon reaction. These photochromic molecules show unique nonlinear photo-response. Only the short-lived transient colored species are formed by illumination with weak light, whereas the excitation with high power CW light generates the long-lived transient colored species. Although high power pulse lasers were necessary to induce conventional simultaneous and stepwise two-photon absorption processes, the stepwise two-photon absorption process with the fast photochromic compound can be initiated by extremely weak continuous wave (CW) LEDs.

We will develop nonlinear visible-light responsive photochromic molecules that can work only under high-power CW light and exclude the influence of background light.

【Research Methods】

In this research project, we will focus on the development of the innovative photochromic molecules capable of visible-light excitation and wavelength selective excitation by combining the fast photochromism, the stepwise photochromism, and the stepwise photochromism via higher excited state. The first objective is to realize the nonlinear photochromic reaction upon the excitation with visible light between 400 and 600 nm, and the final

goal is set to achieve the stepwise photochromic reaction with visible light longer than 650 nm or near infrared pulse light.

【Expected Research Achievements and Scientific Significance】

A reverse saturable absorber (RSA) is a material whose absorption coefficient would increase with increasing the excitation light intensity. On the other hand, a material whose absorption coefficient would decrease when the excitation light intensity increases is known as a saturable absorber (SA). Nonlinear photo-responsive photochromic molecules changing their color from colorless to colored (positive photochromism) upon high-power UV LED can be considered as RSAs. On the other hand, those changing their color from colored to colorless (negative photochromism) can be regarded as SAs. We expect the RSA and SA properties induced without the use of high power laser source can be applied to unique optical shutters and optical filters.

【Publications Relevant to the Project】

- Y. Kobayashi, T. Katayama, T. Yamane, K. Setoura, S. Ito, H. Miyasaka, J. Abe, "Stepwise two-photon induced fast photoswitching via electron transfer in higher excited states of photochromic imidazole dimer", *J. Am. Chem. Soc.*, **138**, 5930-5938 (2016).
- K. Mutoh, Y. Nakagawa, A. Sakamoto, Y. Kobayashi, J. Abe, "Stepwise two-photon-gated photochemical reaction in photochromic [2.2]paracyclophane-bridged bis(imidazole dimer)", *J. Am. Chem. Soc.*, **137**, 5674-5677, (2015).

【Term of Project】 FY2018-2022

【Budget Allocation】 149,700 Thousand Yen

【Homepage Address and Other Contact Information】

<http://www.chem.aoyama.ac.jp/Chem/ChemHP/phys3/top/abe.html>



Title of Project : Clarification of Ubiquitous Proton Function in Photoreceptive Proteins by Quantum Molecular Dynamics Simulations

Hiromi Nakai

(Waseda University, Faculty of Science and Engineering, Professor)

Research Project Number : 18H05264 Researcher Number : 00243056

Keyword : Photoreceptive proteins, Quantum molecular dynamics, Ubiquitous protons, DC-DFTB-MD

【Purpose and Background of the Research】

Biological molecules possess the sophisticated mechanisms for achieving functions as a result of the long-time evolution. At the atomic level, protons ubiquitously exist in biological systems in various forms, and show heterogeneous dynamical behavior coupling with the electron-state changes and structural changes in the surrounding environment. The resulting proton transfers play a vital role in the mechanisms for achieving functions on life phenomena. Therefore, in order to elucidate the mechanisms for achieving functions in biological systems at the atomic level, it is important to correctly understand the dynamical behavior of ubiquitous protons.

In experimental studies, various structures of biological molecules have been determined from x-ray crystallography and cryo-electron microscopy. However, the positions and dynamical processes of protons have not been observed due to the limit of the temporal and spatial resolution. In theoretical studies, although chemical reactions have been analyzed with quantum molecular dynamics (QMD), the tractable number of atoms is limited to at most one thousand due to the high computational cost. Thus, elucidating the dynamical behavior of ubiquitous protons is significantly difficult.

In the present study, the microscopic mechanisms of life phenomena will be clarified using our original large-scale QMD.

【Research Methods】

Our original QMD, divide-and-conquer-type density-functional tight-binding molecular dynamics (DC-DFTB-MD), is further improved in combination with GPU accelerator. Extension of this method for excited states is also performed.

As an application to photoreceptive proteins, ubiquitous proton transfers in bacteriorhodopsin (BR), which has the function of light-driven proton pump, are analyzed. From DC-DFTB-MD of BR with lipid bilayer and water (Figure 1), multiple proton transfers on the photocycle are fully observed, and the microscopic origin of the unidirectional and active proton transport in BR resulting in light-energy conversion is elucidated.

In addition to BR, ion-transporting microbial

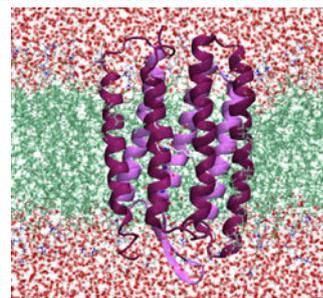


Figure 1. All-atom model of BR (~50,000 atoms).

rhodopsins and ATP synthase are targets of the present study. The microscopic mechanisms of various biological functions in these systems are clarified from the viewpoint of ubiquitous protons.

【Expected Research Achievements and Scientific Significance】

Theoretical basis of revealing the dynamical behavior of ubiquitous protons in arbitrary biological systems is constructed. Moreover, it is expected that we can gain microscopic insights into the essence of life phenomena involving chemical reactions and develop the biological materials with high efficiency.

【Publications Relevant to the Project】

- “Three pillars for achieving quantum mechanical molecular dynamics simulations of huge systems: Divide-and-conquer, density functional tight-binding, and massively parallel computation” H. Nishizawa, Y. Nishimura, M. Kobayashi, S. Irle, and H. Nakai, *J. Comput. Chem.*, **37**, 1983 (2016).
- “Rigorous pKa Estimation of Amine Species Using Density-Functional Tight-Binding-Based Metadynamics Simulations” A. W. Sakti, Y. Nishimura, and H. Nakai, *J. Chem. Theory Comput.*, **14**, 351 (2018).

【Term of Project】 FY2018-2022

【Budget Allocation】 151,100 Thousand Yen

【Homepage Address and Other Contact Information】

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Title of Project : Exploring Interface Science by Concerted Use of Advanced Spectroscopy and Theory

Tahei Tahara
(RIKEN, Cluster for Pioneering Research, Chief Scientist)

Research Project Number : 18H05265 Researcher Number : 60217164

Keyword : Interface, Nonlinear Spectroscopy, Ultrafast, MD Simulation, Molecular Science

【Purpose and Background of the Research】

Although interfaces play crucial roles in many areas of science and technology, our understanding of interfacial phenomena is insufficient. In this research, researchers who have been developing new experimental and theoretical methodologies collaborate and promote research on liquid interfaces. We clarify static and dynamic processes at the interfaces and elucidate their mechanisms at the molecular level.

【Research Methods】

By using phase-controlled interface selective nonlinear spectroscopy and molecular dynamics simulation, we investigate liquid interfaces by focusing on the following three issues.

(1) Ultrafast interfacial vibrational dynamics

Elucidation of the ultrafast phenomena is the frontier of science. In particular, elucidation of ultrafast dynamics of the hydrogen bonding is essentially important. Ultrafast hydrogen-bond dynamics of bulk water has been intensively studied, but the dynamics at the interface is not elucidated. We investigate it by femtosecond time-resolved phase-controlled sum-frequency generation spectroscopy and its extension to two-dimensional spectroscopy.

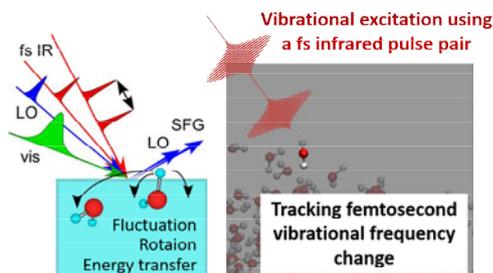


Figure 1 Ultrafast dynamics at liquid interfaces

(2) Structure of liquid interfaces and reactions

Reactions at the liquid interface are thought to be different from those in the solution, but it has not been clarified. We elucidate the structure of liquid interfaces and clarify their effects on the reactivity of interfacial molecules. Furthermore, we observe the interfacial reaction process by the time-resolved measurement directly.

(3) Buried interfaces and complex real interfaces
"Buried interfaces" such as solid/liquid interfaces are an unexplored area. We elucidate the properties of the buried interfaces at the molecular level, from oxide/water interfaces to complex interfaces that are widely utilized in the real world such as the electrode interface.

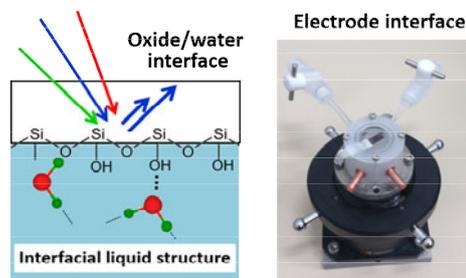


Figure 2 Buried interface and real complex interface

【Expected Research Achievements and Scientific Significance】

The outcomes of this research not only greatly advance interfacial science, but also provide solid basis to a wide range of science and technology including environmental chemistry and electrochemistry where interfacial phenomena play major roles.

【Publications Relevant to the Project】

- Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. Ultrafast dynamics at water interfaces studied by vibrational sum-frequency generation. *Chem. Rev.* **2017**, *117*, 10665-10693.
- Ishiyama, T.; Imamura, T.; Morita, A. Theoretical studies of structures and vibrational sum frequency generation spectra at aqueous interfaces. *Chem. Rev.* **2014**, *114*, 8447-8470.

【Term of Project】 FY2018-2022

【Budget Allocation】 148,400 Thousand Yen

【Homepage Address and Other Contact Information】

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