RESEARCH ACTIVITIES
Materials Molecular Science

Extensive developments of new functional molecules and their assemblies are being conducted in three Divisions of Electronic Structures, Electronic Properties, and Molecular Functions, and one division for visiting professors and associate professors, in an attempt to discover new phenomena and useful functions. The physical (electric, optical, thermal and magnetic) properties on new functional materials, the chemical properties like enzymes, catalysis and photochemistry, the exploitation of new spectroscopic methods for materials molecular science, and technological applications like batteries, photocatalysts, fuel cells, solar cells and field effect transistors are investigated in this department.
Exploitation of Novel Spectroscopic Methods for Material and Surface Science

For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed in situ x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The apparatus is extensively open for public usage. Recently, assistant professor Kohei Yamamoto is developing the reflectance soft x-ray photoelectron spectroscopy system installed at Beamline 07LSU of SPring-8. Moreover, we designed and constructed the subsecond time resolved AP-HAXPES measurement system, and successfully investigated electrochemical reaction dynamics for the cathode Pt oxidation/reduction and the S₂-adsorption/desorption processes upon an abrupt step of the cathode-anode bias voltages. These works were supported by the NEDO Fuel Cell project. More recently, assistant professor, Takanori Koitaya, has been investigating various kinds of surface chemical reactions such as methane activation and CO₂ hydrogenation using the AP-HAXPES system combined with the near ambient pressure soft x-ray photoelectron spectroscopy system installed at Beamline 07LSU of SPring-8.

The second subject is the x-ray absorption fine structure (XAFS) investigation. This includes femto- and picosecond time resolved XAFS measurements using the x-ray free electron laser SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic thin films with the atomic layer resolution scale.

The third subject is the x-ray absorption fine structure (XAFS) investigation. This includes femto- and picosecond time resolved XAFS measurements using the x-ray free electron laser SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic thin films. Moreover, conventional temperature dependent extended x-ray absorption fine structure (EXAFS) spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of alloy systems.

Selected Publications

1. Operando Characterization of Copper-Zinc-Alumina Catalyst for Methanol Synthesis from CO₂ and H₂ by AP-HAXPES

Operando spectroscopy is a very powerful tool for the characterization of heterogeneous catalysts under working conditions. In this study, an AP-HAXPES investigation of an industrial copper-zinc-alumina methanol synthesis catalyst was performed using our AP-HAXPES system shown in Figure 1(a) to reveal surface chemical states of the catalyst and adsorbed intermediates during the catalytic reaction. The reaction activity of the present catalyst is quite important because of the significance of the CO₂ circulation. In-situ formation of metallic Cu-Zn particles was detected during the reduction process of the catalyst under hydrogen atmosphere. More interestingly, a significant amount of Al atoms was found to be incorporated into ZnO during H₂ reduction and also CO₂ hydrogenation chemical reaction as seen in Figures 1(b) and 1(c).

In this study, we also installed a quadrupole mass spectrometer installed in the differentially pumped electron lens chamber to observe the reaction products in the presence of near ambient-pressure CO₂ and H₂ gases. The formation of CO and methanol was actually observed very clearly. Temperature dependence was found to differ between rWGS (reverse water-gas shift to form CO) reaction and methanol synthesis; the reaction products of rWGS monotonically increased as a function of the sample temperature between 420 K and 593 K, whereas the rate of the methanol synthesis reached a local maximum at 480 K, and decreased at 593 K. The observed temperature-dependence of methanol synthesis correlates well with the dynamic changes in the chemical states of the catalyst and adsorption intermediates during the reaction observed in the AP-HAXPES.

Figure 2 shows the C 1s and O 1s HAXPES during the CO₂ hydrogenation reaction. The total environmental pressure amounts 53 kPa. Although the C 1s spectra measurement was rather difficult due to the small C 1s photoionization cross section, important reaction intermediate species such as CO₃(a), HCOO(a), and CH₃O(a) are seen, implying successful direct observation in the present catalytic reaction. Schematic surface reaction model is also shown in the figure.

2. Exploitation of Reflectance Soft X-Ray Magnetic Circular Dichroism System for the Clarification of Layer-Resolved Magnetic Structures

Magnetic thin films/multilayers with complex depth structures exhibit a wide variety of magnetic phenomena due to the interactions between layers. Furthermore, multilayer structures have been used to realize useful properties in recording media, which is an important application of magnetic materials. Direct observation of the magnetic distribution in the depth direction of such magnetic multilayers has been used to elucidate the mechanism of evolution of magnetic structures in thin films. We installed an experimental setup for reflectance x-ray magnetic circular dichroism (XMCD) method in the soft X-ray regime at UVSOR BL4B and experiments were performed on test samples. The sample was CoFeB and an oscillating structure was observed due to the interference of the cap layer and the underlying layers. We observed the difference corresponding to XMCD by changing the direction of magnetic field, which is consistent with the simulation results. We also conducted spectroscopic measurements and obtained photon energy and reflection angle dependence to analyze the depth-resolved magnetization information. We will test the silicon drift detector for getting information of higher angle regions and eliminating the fluorescence effect with energy selectivity.

Reference
Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down configuration) is a key structural parameter that determines unique physicochemical properties of interfacial water systems. Nevertheless, orientation of water molecules, i.e., configuration of hydrogens, in the interfacial hydrogen-bond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning probe microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

We have used heterodyne-detected sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that Imχ(2) SFG spectra (χ(2): The second-order nonlinear susceptibility) obtained by the heterodyne detection exhibit positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, the heterodyne-detected Imχ(2) SFG has a great advantage to direct observation of water orientation that cannot be investigated through other traditional experimental methods. With this sophisticated molecular spectroscopy technique, we have conducted a series of pioneering research on unique structures and physicochemical properties of hydrogen bonds of interfacial water molecules.

Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications
1. Critical Impacts of Interfacial Water on the Photocatalytic C–H Conversion of Methane

On-site and on-demand photocatalytic methane conversion under ambient conditions is one of the urgent global challenges for the sustainable use of ubiquitous methane resources. However, the lack of microscopic knowledge on its reaction mechanism prevents the development of engineering strategies for methane photocatalysis. Combining real-time mass spectrometry and operando infrared absorption spectroscopy with ab initio molecular dynamics simulations, here we report key molecular-level insights into photocatalytic green utilization of methane. Activation of the robust C–H bond of methane is hardly induced by the direct interaction with photogenerated holes trapped at the surface of photocatalyst; instead, the C–H activation is significantly promoted by the photoactivated interfacial water species (Figure 1). The interfacial water hydrates and properly stabilizes hydrocarbon radical intermediates, thereby suppressing their overstabilization. Owing to these water-assisted effects, the photocatalytic conversion rates of methane under wet conditions are dramatically improved by typically more than 30 times at ambient temperatures (~300 K) and pressures (~1 atm) in comparison to those under dry conditions. This study sheds new light on the role of interfacial water and provides a firm basis for design strategies for non-thermal heterogeneous catalysis of methane under ambient conditions.

2. Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water

Environmentally sustainable and selective conversion of methane to valuable chemicals under ambient conditions is pivotal for the development of next-generation photocatalytic technology. However, due to the lack of microscopic knowledge about the non-thermal methane conversion, controlling and modulating photocatalytic oxidation processes driven by photogenerated holes remain a challenge. Here, we report novel function of metal cocatalysts to accept photogenerated holes and dominate the oxidation selectivity of methane (Figure 2), which is clearly beyond the conventional concept in photocatalysis that the metal cocatalysts loaded on the surfaces of semiconductor photocatalysts mostly capture photogenerated electrons and dominate reduction reactions exclusively. The novel photocatalytic role of metal cocatalysts was verified by operando molecular spectroscopy combined with real-time mass spectrometry for metal-loaded Ga$_2$O$_3$ model photocatalysts under methane gas and water vapor at ambient temperature and pressure. Our concept of metal cocatalysts that modulate photocatalytic oxidation as well as reduction opens a new avenue for controlling photocatalytic redox reactions by metal-cocatalyst engineering.

3. Monolayer-Sensitive Coherent Raman Spectroscopy for Molecular Systems on Conductive Surfaces

Highly sensitive and versatile spectroscopy for molecular systems on conductive surfaces, relating with electrochemistry, corrosion processes, and catalytic reactions is crucial in many scientific and technological fields. However, conventional spectroscopy based on spontaneous Raman scattering requires some specific electronic/plasmonic enhancements due to its weak signal, imposing serious restriction on the system to which it is applied. Here, we introduce a monolayer-sensitive and versatile stimulated Raman spectroscopy without using any electronic/plasmonic enhancements. This spectroscopy innovation is achieved by coherent anti-stokes Raman scattering (CARS) with dramatical improvement of signal-to-noise ratio based on an optimally shaped time-delayed pulse; our stimulated and time-resolved Raman observation scheme not only enhance the vibrational signal but also significantly suppress the huge background from conductive surfaces, which is demonstrated by focusing on well-defined self-assembled monolayers on flat gold substrates.

References

Organic Solar Cells

Department of Materials Molecular Science
Division of Molecular Functions

HIRAMOTO, Masahiro
Professor
[hiramoto@ims.ac.jp]

Education
1984 B.E. Osaka University
1986 Ph.D (Engineering) Osaka University

Professional Employment
1984 Technical Associate, Institute for Molecular Science
1988 Research Associate, Osaka University
1997 Associate Professor, Osaka University
2008 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Awards
2021 Outstanding Achievement Award, Molecular Electronics & Bioelectronics Division, Japan Society of Applied Physics
2017 Fellow Award of Japan Society of Applied Physics
2006 Paper award, Molecular Electronics & Bioelectronics division, Japan Society of Applied Physics
2006 Research and Education Award, Osaka University
2004 Editor Award, Japanese Journal of Applied Physics


Keywords
Organic Semiconductors, Up-Conversion, Lateral Junction

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, etc. Followings are our recent results. (1) Photon up-conversion (UC) from near infrared (NIR) to visible yellow (Figure 1) by utilizing charge transfer (CT) states at donor/acceptor (D/A) interface of organic solar cells. (2) A novel concept of the structure of organic solar cell, namely, a lateral junction in which the photogenerated holes and electrons are laterally transported and extracted to the respective electrodes. Even 1.8 cm-length lateral cells (Figure 2) showed clear photovoltaic behavior. (3) The reduction of open-circuit voltage ($V_{oc}$) loss due to non-radiative recombination in organic solar cells by using high-mobility organic semiconductors. The $V_{oc}$ reaching to thermodynamic (Shockley-Queisser) limit was observed. (4) The ppm-level doping effects in organic semiconductor films and organic single crystals for organic solar cells. So far, we have reported complete $pn$-control, doping sensitization, and the ppm-level doping effects using an ultra-slow deposition technique reaching $10^{-9}$ nm s$^{-1}$ (Figure 3) in organic rubrene single crystals measured by the Hall effect, which shows a doping efficiency of 82% comparable to the B in Si. These results can be regarded as a foundation for the construction of highly efficient organic solar cells.

Selected Publications


Figure 1. Up-converted (UC) yellow emission by star-shaped near infrared irradiation.

Figure 2. Picture of a 1.8 cm-length lateral cell.

Figure 3. Ultra-slow co-deposition technique to produce the doped rubrene single crystal for Hall effect measurements.
1. Efficient Interfacial Up-Conversion Enabling Bright Emission with Extremely Low Driving Voltage in Organic Light-Emitting Diodes\textsuperscript{1)}

We reported the photon up-conversion (UC) from near infrared (NIR) to visible yellow (Figure 1).\textsuperscript{21} The UC emission occurs by the combination of organic solar cell process and up-conversion (UC) process (Figure 4(b)). Double layer consists of rubrene donor (D) and non-fullerene acceptor (A) was used. In the solar cell process, the free charges are generated at D/A interface by near-infrared (NIR) excitation. In the UC process, the charge recombination at the D/A interface takes place and triplet states (T\textsubscript{1}) are formed in the rubrene film through the CT states. Finally, the UC emission occurs by the T–T annihilation.

The UC process can also occur by the injected electrons and holes from the electrodes. So, we could fabricate the up-converted organic EL device. Red EL of 2.0 eV could be emitted by applied voltage of half energy of 1.0 V by utilizing up-conversion (Figure 4(a)). 100 cd/m\textsuperscript{2} at 1.5 V and 1000 cd/m\textsuperscript{2} at 2.5 V were obtained. A battery of 1.5 V was enough for EL operation. This is the world lowest operating voltage reported so far. Thus, the CT state, which is an essence of organic solar cell process, can be also utilized for up-converted organic EL.

2. Monolayer-Digitized Band Mapping for Doped Rubrene Single Crystals\textsuperscript{3)}

The band mapping for doped rubrene single crystals by using Atomic/Kelvin force microscopy (AFM/KFM) was performed. The ppm-level doping technique using ultra-slow deposition (Figure 3) was used. Doped rubrene single crystal was obtained by the homoepitaxial growth on rubrene single crystal substrate. Mo\textsubscript{3}O\textsubscript{9} (1,000 ppm) was used as an acceptor dopant. Thicknesses of doped homoepitaxial layers were varied from 0 to 20 nm.

Morphological and potential images of doped homoepitaxial rubrene are shown in Figures 5(a) and 5(b). The island image (AFM) (Figure 5(a)) and the simultaneously obtained potential image (KFM) (Figure 5(b)) are roughly coincided. The average work functions of 3 and 4 rubrene monolayers were determined to 4.18 and 4.22 eV, respectively. Thus, we could plot the relationship between work function and number of rubrene monolayer (Figure 5(c), blue dots).

For Mo\textsubscript{3}O\textsubscript{9} (1,000 ppm) doped rubrene single crystal, the number of negatively ionized acceptors of $2.0 \times 10^{18}$ cm\textsuperscript{-3} and the doping efficiency of 3.3% were calculated by the band mapping. Specific values of work function observed for each number of rubrene monolayer suggests that the built-in potentials are monolayer-digitized.

References


Awards
IZAWA, Seiichiro; NF Foundation R&D Encouragement Award (2021).
IZAWA, Seiichiro; The 11th Young Scientist Award of National Institutes of Natural Sciences (2022).
IZAWA, Seiichiro; The Morino Foundation for Molecular Science (2022).
In order to elucidate functions of molecules, characterization of the molecule is the first step. There is a variety of important molecules, which are insoluble in any solvents and functional at amorphous state. Solid-state NMR enables us to obtain a variety of information at atomic resolution without damage to molecules and significant restrictions. Thus, solid-state NMR is one of the essential tools for the characterizations of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their application to structural biology and materials science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterization of those molecules based on solid-state NMR is underway through collaborations with several research groups.

Selected Publications
1. Structural Characterization of Protein Using Solid-State NMR

Water bear possess extreme tolerance for environments. So far, the molecular mechanisms to protect their cells in such environments have not been clarified yet. Especially, under extremely dry environment, water bear takes torpor, then recovers under wet environment. It has been reported that several specific proteins have been expressed in water bear before torpor. Secretary abundant heat soluble protein (SAHS) is one of those proteins, and its biological functions have not been clarified yet. However, it has been considered that SAHS plays important roles to conserve their tissues, thus cells of water bear during torpor. The molecular structure of SAHS under hydrated state has been characterized precisely. In contrast, their structural information is limited under dry state. Therefore, we have been attempted to clarify the SAHS structure at dry state using solid-state NMR spectroscopy. This is collaboration project with Prof. Kato group in IMS and Prof. Yagi group in Nagoya city university.

Any proteins under dry condition may be expected to exhibit inhomogeneous structure. In order to investigate local structural and those homogeneity of SAHS at dry state, 2D dipolar assisted rotational resonance (DARR) $^{13}$C-homo-nuclear correlation solid-state NMR measurements were carried out for the dry-state SAHS protein which only isoleucine residues are isotopically enriched by $^{13}$C and $^{15}$N. Those samples were newly prepared by improved procedures. Together with solid-state NMR analyses for several mutants for SAHS, signal assignments were successfully achieved. Then local secondary structures were identified through investigations of obtained $^{13}$C chemical shifts of individual sites. Consequently, the result suggests that essentially most of secondary structure of SAHS are conserved even under dry state.

2. Developments of Spectral Editing Solid-State NMR Techniques

For the characterization of molecules using NMR, signal assignment is the first important step. Especially for biomolecules, such as proteins, $^{13}$C and $^{15}$N uniform isotope enrichments of samples is common and essential approach. Those isotope enrichments of samples enable to detect homo-, and heteronuclear correlation peaks among $^{13}$C and $^{15}$N nuclei at reasonable sensitivities. Those analyses enable structural characterizations of molecules. However, those isotope enrichments are not generally applicable, such as natural products and synthetic molecules via complicated processes. For such unlabeled samples, the efficient approach is quite limited due to the difficulties of observation of $^{13}$C and $^{15}$N correlation signals among natural abundant nuclei. Therefore, totally different approaches must be applied for their characterizations.

We have been working on developments of efficient spectral editing techniques to support accurate signal assignments for such unlabeled organic samples in solid-state NMR spectroscopy under both rigid and mobile sample conditions. The applicability of the developed technique has been verified for reference samples and their applications are under study.

3. Development of Solid-State NMR Probes

We have been working on developments of totally original solid-state NMR probes during a couple of years. In those probes, only spinning module and spinning counting module are remained as commercial parts. In order to replace those remained commercial parts to our original ones, we have been working on developments of original sample spinning modules for magic angle spinning (MAS) solid-state NMR probes which are fully compatible with currently using Bruker spectrometer and commercial sample tubes. As an initial stage, we started the design of a spinning module for standard 4.0 mm sample tube for Bruker. After two times of version up, our original spinning module reached to the spinning performance of commercial one from Bruker. The experimental performance of developed spinning module was evaluated by installing the module to the originally developed bench spinner system. By using Bruker automated spinning controller using standard parameters of drive- and bearing gas pressures for commercial 4.0 mm sample tube, our spinning modules achieved maximum sample spinning rate of 15 kHz for Bruker commercial sample tube. In addition, by using originally built manual spinning controller system with original drive- and bearing-gas pressures, our spinning module achieved higher spinning rate over maximum spinning rate for Bruker commercial spinning module. Currently, a shrink version of the spinning module is under development in order to enable installation of the module to a narrow bore solid-state NMR probe with outer sleeve diameter of 38 mm.
Hydrogen has a charge flexibility and can take various charge states such as proton (H⁺), atomic hydrogen (H₀), and hydride (H⁻) depending on the different bonding states in materials. Due to this feature, whereas hydrogen diffusing in metals behaves a state close to H₀, H⁺ becomes the charge carrier in many types of chemical compounds, including polymer, solid acid, MOF, and ceramics. In the former case, hydrogen absorbing alloys and hydrogen embrittlement of metals have been studied, and in the latter case, materials research for fuel cell applications has been actively carried out over the past few decades. In contrast, H⁻ is a relatively rare state that can only be taken when hydrogen is coordinated to metals with low electronegativity such as alkali metals and was not well recognized as a charge carrier. Therefore, even though H⁻ has attractive features such as suitability for fast ionic conduction in terms of size, valence, and polarization and strong reduction properties (E°(H⁻/H₂) = −2.35 V vs. SHE), its electrochemical applications have not been considered. Against this background, we developed a series of H⁻ conductive oxyhydrides, La₂₋ₓSrₓLiH₁₋ₓO₃₋ₓ, in 2016 and found its function as an H⁻ solid electrolyte for the first time. Based on the results, our group is challenging the progress of materials science on H⁻ conductors and the development of novel electrochemical devices utilizing H⁻ conduction phenomena.

Selected Publications

1. Study on H⁻ Conductive Oxyhydrides¹⁻⁴)

In 2016, we synthesized a series of K₂NiF₄-type oxyhydrides, La₂₋ₓSrₓLiH₁₋ₓO₁₋₀.₃₋₂₇ (LSLHO), which are equipped with anion sublattices that exhibit flexibility in the storage of H⁻, O²⁻, and vacancies (Figure 2 upper) and demonstrated pure H⁻ conduction properties in the oxyhydrides.¹) The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state Ti/LSLHO/TiH₂ cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using H⁻ conduction phenomena.

Based on elemental substitutions to LSLHO, we have been exploring hydride ion conducting oxyhydrides. As shown in Figure 2, we have found that the H⁻ and O²⁻ arrangement in the K₂NiF₄-type structure can be controlled by tuning the valence (electrostatic valence rule) and size balance of the cation species (tolerance factor). More recently, we reported a new H⁻ conductive oxyhydride, Ba₁₋₀.₅LiH₂₋₀.₉O₀.₉ (BLHO), containing a high amount of barium and hydrogen vacancies and exhibiting long-range ordering at room temperature. Increasing the temperature above 315 °C disorders the long-range ordering, triggering superionic conduction with a high H⁻ conductivity of over 0.01 S·cm⁻¹ nearly independent of the temperature. The finding of the H⁻ superionic conductor operating intermediate temperature range, which might open possibilities for new electrochemical device.

Figure 2. Comparison of the crystal structures of H⁻ conductive oxyhydrides La₂₋₋ₓSrₓLiH₁₋ₓO₁₋ₓ₋₀.₃₋₂₇ (x = 0, y = 0, 1, 2) and Ba₂₋₋ₓMₓH₀.₉O₀.₉₋ₓ (M = Sc, Y).

Synthesizing oxyhydrides usually requires unique methods such as high-pressure reactions, and topochemical reactions using CaH₂ reductant. Since the former method is a sealed reaction system, loss of light elements, such as hydrogen, can be prevented, making it a suitable synthesis method for composition control and, ultimately, exploration for new materials. On the other hand, the latter is an O²⁻/H⁻ exchange reaction and is useful for preparing metastable phases. However, the high-pressure method and the topochemical reaction have each problem of low synthesis volume and low reproducibility, respectively. To expand the research on hydride ionic conductors to the development of electrochemical devices, it is necessary to establish a simple and large volume synthesis process for the constituent materials. We have been trying to establish a suitable synthesis method for oxyhydrides to resolve the above problems.

For the K₂NiF₄-type oxyhydrides, we have successfully established the solid-state reaction method under ambient-pressure.⁵,⁶) Furthermore, we have succeeded in direct synthesis of barium titanium oxyhydride BaTiO₃.Hₓ by mechanochemical reaction, allowing gram-scale and speedy preparation of the functional material. Its unique reaction condition without external heating might be suitable for materials exploration of transition metal oxyhydrides. We also confirmed that the prepared polycrystalline BaTiO₃.Hₓ worked as a hydrogen-permeable electrode. This result suggests that H⁻/e⁻ mixed conducting oxyhydrides are promising for electrode use in electrochemical chemical/energy conversion devices (Figure 4).

Figure 4. BaTiO₃.,Hₓ synthesized by a mechanochemical method and its performance as hydrogen permeable electrodes.

2. Materials Processing of Oxyhydrides for Electrochemical Applications⁵⁻⁷)

References

Awards
KOBAYASHI, Genki; The NAGAI Foundation for Science & Technology Academic Award (2022).
OKAMOTO, KEI; Student Presentation Award, The Electrochemical Society of Japan (2021).
Physical properties and elementary processes at the interface between electrode and electrolyte are strongly related to the performance of energy devices. Traditionally, the physical properties and elementary processes have been indirectly discussed based on the changes of the device performances. Developments of the techniques of spectroscopic measurements have analyzed the physical properties and elementary processes at the interface. In addition to the spectroscopic analysis, direct imaging and nano/atomic-scale analysis by microscopic measurements of the interface will reveal the real nature of the interface.

Historically, scanning probe microscopy (SPM) have been developed as the experimental technique to analyze the physical properties and elementary process in nano/atomic-scale in ideal conditions such as ultra-high vacuum and low temperature for single crystal samples. We have constructed SPM systems to analyze the physical properties and elementary process at electrode/electrolyte interface (Figure 1).

At the interface between electrode and electrolyte of rechargeable battery during the charge and discharge reactions, solvent molecules, carrier ions and additives congregate and form specific states. The properties of interface phases are related to the battery performances (capacity, cyclability, rate performance etc.), however, much is unknown at the interface. We have investigated the mechanical properties at the interface. Figure 2 shows force curves obtained by the SPM with changing the electrode potential in an electrolyte for rechargeable battery. At open circuit potential (OCP), the adhesion force (negative force in the force curve) was negligible value. By changing the potential to $-1.25 \text{ V (vs. Pt)}$, the adhesion force was increased to $-60 \text{ nN}$. Further sweep of the potential to $-2.0 \text{ V}$, the adhesion force was returned to negligible value. These changes of the mechanical properties are caused by the changes of the interface phases by applied electric fields that relate to the battery performance.

Figure 2. Force curves obtained by the electrochemical SPM systems at the interface between an electrolyte for rechargeable battery and the electrode with changing the sample potential. The black, red and gray curves were obtained at open circuit potential (OCP) $=-0.1 \text{ V}$, $-1.25 \text{ and } -2.0 \text{ V}$, respectively. Inset (a); the change of the adhesion force obtained by the SPM by changing the potential. Inset (b); an SPM image at $-1.25 \text{ V}$ (300 nm × 300 nm in $xy$ scales and 0 ~ 180 nm in $z$ scale). All potential is defined from the difference from Pt.

References
Visiting Professors

Visiting Professor

TANAKA, Koichiro (from Kyoto University)

Ultrafast Laser Spectroscopy and Terahertz Optical Sciences

In recent years, the technology of ultra-short lasers and terahertz light has made remarkable progress, revealing unprecedented ultra-non-equilibrium physics and order formation of solid materials under high-intensity light irradiation. We make full use of such state-of-the-art optical technology to study the excited state dynamics of semiconductors, single-layer materials, photonic crystals, and metamaterials, as well as “non-equilibrium physics under high-intensity light fields.” We are also looking for ways to bring out new physical properties by utilizing the interaction between light and matter. Specific research topics include (1) elucidation of non-equilibrium physical properties of solids in high-intensity light fields, (2) research on ultrafast nonlinear phenomena using ultrashort pulse lasers, and (3) new spectroscopy using terahertz light, (4) optical properties of monoatomic layer materials, (5) research on exciter quantum effects in semiconductors, etc.

Visiting Professor

OSAKA, Itaru (from Hiroshima University)

π-Conjugated Polymers for High-Efficiency Organic Photovoltaics

Organic photovoltaics (OPVs) have been attracting much attention due to lightweight, flexible, low-cost and low-energy solution-processability. Improving the power conversion efficiency is one of the important issues in OPVs. We designed and synthesized a series of π-conjugated polymers based on an extended fused ring, named dithienonaphthobisthiadiazole. The polymers had rigid and coplanar backbone structure, which resulted in high-crystalline structure in the thin film. The efficiency of the photovoltaic cells was as high as 12% when one of the polymers was combined with a fullerene acceptor, which was among the highest values for polymer/fullerene cells. Importantly, extremely high fill factors of over 0.8 were obtained, which was likely ascribed to the high charge carrier mobility. In addition, when another dithienonaphtobisthiadiazole-based polymer was combined with a nonfullerene acceptor, it showed high efficiencies of over 16%. Moreover, the polymer showed high photocurrent generation even with very small driving force energy. These results would be important guidelines for the development of high-performance polymers.

Visiting Associate Professor

AKIMOTO, Ikuko (from Wakayama University)

Pulsed EPR Spectroscopy of Electron and Hole Spins in Semiconductor Crystals

The coexistence of electrons and holes in semiconductors provides the functionality of optoelectronic devices, such as photo sensors, solar cells, and organic light emitting diodes (OLEDs). A microscopic understanding of the underlying physics of electron–hole interaction is essential for further development of devices. The pulsed electron–electron double resonance (DEER or PELDOR) technique, a pump–probe measurement of two-spin interactions, has been established to analyze the distance between separated spin labels in a molecule. However, it is challenging to apply this technique to the randomly distributed spin systems that are typically realized in optoelectronic devices. We have investigated the spin interactions between randomly distributed electron and hole traps created by optical excitation in a semiconductor by the DEER technique using arbitrary-waveform pulses of Gaussian and chirped rectangular microwave pulses. Adiabatic excitation of the spin system extracted widely distributed interacting distances of 3–4 Å, indicating reasonable values before tunneling recombination, from the vast background interactions.