



Materials research Center for Element Strategy

Materials Research Center for Element Strategy



Tokodai Institute for Element Strategy



Tokyo Tech

Tokyo Institute of Technology

Materials Research Center for Element Strategy (MCES)

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Members

August, 2019

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	Soushi Iimura	(203)
	Junghwan Kim	(203)
	Hideya Kumomi	(301, PM of TIES Project)
	Toshiharu Yokoyama	(204, CTO of Tsubame BHB Co., Ltd.)
	Satoru Fujitsu	(304)
	Takeshi Inoshita	(403)
	Masato Sasase	(205)
	Hiroshi Mizoguchi	(205)
	Fucui Liu	(205, JSPS Research Fellow)
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	Technical support staff:	14
	PhD course students:	8
	Master course students:	21
	Under graduate students:	9
	visiting students:	1

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Message from director

MCES is a center for creating novel materials with high impact on society

Hideo Hosono, Director



Our proposal was adopted by the Ministry of Education, Culture, Sports, Science and Technology's "Elementary Research Project" in June 2012. Then, the Material Research Center for Element Strategy (MCES) was established in August, and in April 2015, a dedicated building with the fifth floor and the first basement floor was completed under the funding approved by Estimated Request. As a result, the first full-fledged elemental strategy base has been launched across the country. In the elemental strategy project, although it is the base of the electronic materials area, the range of the electronic materials is regarded as a useful substance with the function utilizing electrons in the solid, so the creation of new functional materials is the mission of our center. In addition, MCES is expected from the beginning of its establishment to actively carry out industry-academia collaboration on the Suzukakedai Campus. The members of MCES are spread not only at Tokyo Tech but also at the National Institute for Materials Science, High Energy Accelerator Research Organization, Nagoya University, Yamanashi University, Kyushu University, Tohoku University, Kyoto University and so on.

Since its establishment, in addition to the elemental strategy project, we have promoted the first selected project out of the JST ACCEL program, "Material Science and Application of Electrifieds" (2014-2018). The project was successfully completed with a high rating, saying that "more than expected results were obtained". One of the achievements by this project is creation of the ammonia synthesis catalyst that efficiently works under mild conditions. A venture company "Tsubame BHB" was established in April 2017 under the sponsorship by a Governmental fund,

UMI, and Ajinomoto Co., Ltd., with the aim of linking these invention to practical use. The research site was approved for installation on campus. This is the first case where the Tokyo Tech venture company's activity site has been set up on the campus. Currently, Tsubame's lab launched at a building for industry-academia collaboration on the Suzukakedai Campus is active for achieving the target keeping close but complementary relationship with MCES.

In addition to being a domestic base for elemental strategy research, we are promoting international joint research. Our proposal to perform collaborated research with University College London (leader: Alexander Shluger) of UK and McGill University (Peter Grutter) of Canada was accepted in the Core-to-Core Program of the Japan Society for the Promotion of Science in 2018. Active joint research has started from 2018 with mutual participation in these three sites.

The "New Element Strategy" is at the forefront of the three priority research areas listed inside and outside of Japan when Tokyo Tech was adopted by a designated national university. The center is required to play an important part of that research. We would like to concentrate on creation of research outputs that have more impact than ever before. Thank you for your support.

Outline of Materials Research Center for Element Strategy

Materials Research Center for Element Strategy (MCES) directed by Professor Hideo Hosono was established on August 1 in 2012 as an independent organization for researches to contribute evolution and revolution of new materials science, under Integrated Research Institute in Tokyo Institute of Technology (Tokyo Tech), and now assigned to one of Strategic Research Hubs.

Since the establishment, MCES has promoted Tokodai Institute for Element Strategy (TIES), a national project for electronic materials, supported by MEXT (Ministry of Education, Culture, Sports, Science and Technology, Japan) Elements Strategy Initiative. MCES also promoted another national project, named ACCEL Program for Materials Science and Application Development of Electrides, supported by Japan Science and Technology Agency from 2013 to 2016.

As introduced above, the promotion of national projects entrusted to Tokyo Tech is one of the primary missions of MCES in addition to the research itself, which includes management of tangibles, financial and human resources, and intangible assets such as intellectual properties like patents in the projects. The other important missions of MCES are promotion of

collaborations with industries which could be priority users of the projects' achievements, and promotion of patent application to minimize patent risks for industry initiators to smoothly commercialize the projects' achievements.

At the moment in April, 2019, over sixty members work with MCES, who are faculty professors and specially appointed professors in Tokyo Tech, visiting professors from the other institutes, postdoctoral research fellows, and skillful technicians. The research activities of the typical researches will be introduced in detail on pages 10-21. The activities of MCES are planned and managed by the steering committee chaired by the Director and constituted by the professors.

The laboratories, facilities, and secretariat of MCES has been mainly located in a dedicated building of Materials Research Center for Element Strategy at Suzukake-dai campus of Tokyo Tech, which was newly constructed in 2015. The building exclusive for MCES has five floors above the ground and one floor under the ground as shown. The building can hold the state-of-the-art facilities for materials researches of Elements Strategy, security spaces for industry collaborations, and a lecture hall.



Research Projects

Tokodai Institute for Element Strategy (TIES)

"Elements Strategy" was born in Japan, 2004, as a vast concept of national policies for creating novel and dream materials by creation of new paradigms in materials science. The concept has grown to generate practical policies as some collaborating national projects sponsored by MEXT and Ministry of Economy, Trade and Industry-Japan, and Japan Science and Technology Agency, incorporating another aspect of replacing rare elements with ubiquitous ones to evade their international supply risks.

In 2012, MEXT started the latest project based on Elements Strategy for ten years, named "Elements Strategy Initiative to Form Core Research Centers" in four fields of magnetic, catalyst and battery, electronic, and structural materials. The project in each field is composed of three research groups: materials creation, analysis and evaluation, and electron theory. The three groups closely collaborate to accelerate research cycles of materials selection, synthesis, and leading-edge measurement and analysis, as schematically represented in Fig. 1. Tokyo Tech was entrusted by MEXT to pursue the research project on the electronic materials, directed by Professor Hideo Hosono as the representative researcher, and established an institute named "Tokodai Institute for Element Strategy (TIES)" under management and promotion by MCES.

In order to promote the research cycle shown in Fig. 1, TIES incorporated researchers from Tokyo Tech, National Institute for Materials Science (NIMS), High Energy Accelerator Research Organization (KEK), and The University of Tokyo. Thus, TIES is a collaborative project among these four institutes (Fig. 2), composed of over one hundred participants. The researches in TIES are lead by Principal Investigators, Group Leaders, and a Planning Manager, who are materials explorers gifted with insightful intuition,

materials scientists exploring leading-edge analysis and evaluation, solid-state physicists having rich talents for physical modeling, and computational scientists leading state-of-the-art computing with materials informatics. They merge and collaborate to maximize the achievements.

The goal of TIES is to open up a new materials science by (1) breaking the spells over old-fashioned

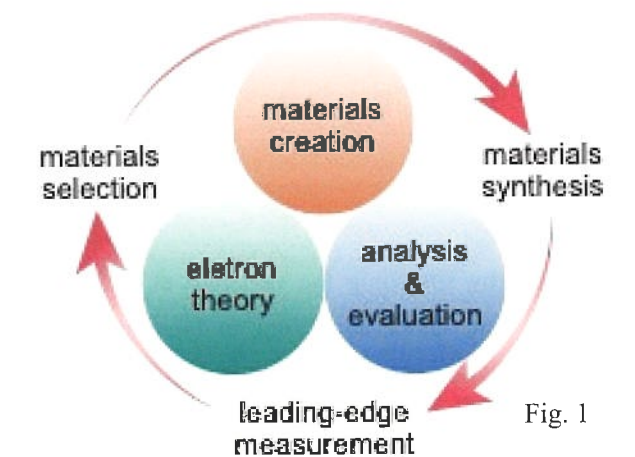


Fig. 1

materials design concepts base on past experiences of successes, (2) exploring the element frontiers of electronic materials, (3) establishing novel materials design and guideline for materials development, and then (4) creating novel and dream but practical materials utilizing abundant and non-toxic elements. For this goal, TIES newly establishes materials science effectively applicable to new and vast material

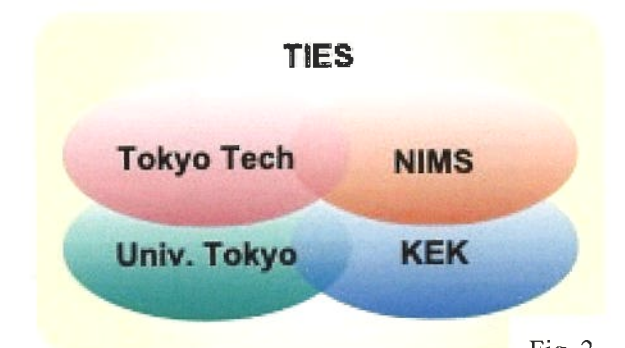


Fig. 2

systems, and explores new routes to develop novel

high-performance and/or low-cost electronic materials without rare and toxic elements, with supports from solid-state physics, computational sciences, and leading-edge analysis. Thus, the scope of TIES spreads over a wide field of any electronic materials which support electronics industry and business, such as semiconductors, superconductors, transparent electrodes, dielectrics, and so on. Especially for semiconductors, ferroelectrics, transparent conductors, and superconductors, which face to urgent issues in terms of resource depletion, environment preservation, and sustainability, TIES focuses on “novel anions”, “unique natural nanostructures”, and “unique electronic structures”.

Toward the goal, TIES divides the whole project period of ten years into three phases, as shown in Fig. 3. In the first phase for three years (2012-2014), TIES executes comprehensive studies of wide material exploration by spreading the variation of materials based on new ideas, structures, and composition, without hesitation to even try rare or toxic elements. Through these challenges, TIES establishes novel concepts of materials design by revealing general laws and concepts which have been hidden beneath interrelations among functions, atomic local structures, and electronic structures of materials, and applicable to wider Material systems than ever. In the second phase for three years (2015-2017), TIES replaces rare or toxic elements in the new materials discovered in the first phase with abundant and nontoxic elements toward Elements Strategy

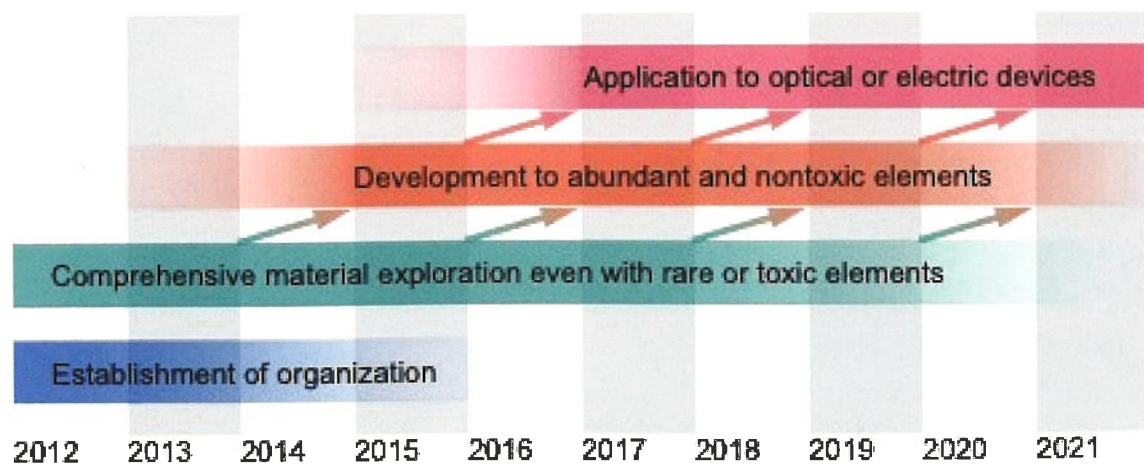


Fig. 3

materials. In the following third phase for four years (2018-2021), TIES steps forward to application researches of the new materials to optical and electrical devices in collaboration with industries, aiming at commercialization of the new materials, along with continuation of the materials exploration of the preceding phases.

At the end of 2014, TIES summarized the achievement of the first phase, and decided for of the focused research areas into which the project resources should be mainly disposed. They are (1) Semiconductors especially for information display applications, (2) Thermally-stable high-k dielectrics/ferroelectrics for power electronics applications, (3) Roles and functionalities of hydrogens in condensed matters, and (4) Enhanced collaboration of electronic theory and materials synthesis for more rapid screening of candidate materials as shown in Fig. 4. With these focused areas, TIES has achieved (1) novel high-performance semiconductors such as bipolar ZrOS, amorphous Zn-Si-O for electron transport, and p-type amorphous Cu-Sn-I systems, (2) high-temperature and high-k non-perovskite dielectrics such as fluorite $\text{HfO}_2\text{:Y}$, silicate $(\text{Bi}_x\text{La}_{1-x})_2\text{SiO}_5$, and Langasite $\text{Ca}_3\text{TaAl}_3\text{Si}_2\text{O}_{14}$, (3) Highly hydrogen sensitive (10^{16} cm^{-3}) quantification apparatus, discovery of hydrides and their functions in amorphous In-Ga-Zn-O and stable hydrides in iron pnictide superconductors, (4) novel nitride semiconductors such as red-light emitting direct-band-gapped CaZn_2N_2 and p-type

$\text{Ca}_3\text{N}_2\text{F}$ for photovoltaics. These new candidate materials and knowledges are now being ready for commercialization in collaboration with many industrial partners in the third phase of TIES.

In 2018, Tokyo Tech placed Element Strategy at the

top of the priority research fields. With the fruitful results of the ten-years project of TIES, the research institute for Element Strategy based on the core research center of MCES will further evolve in the future after the conclusion of TIES.

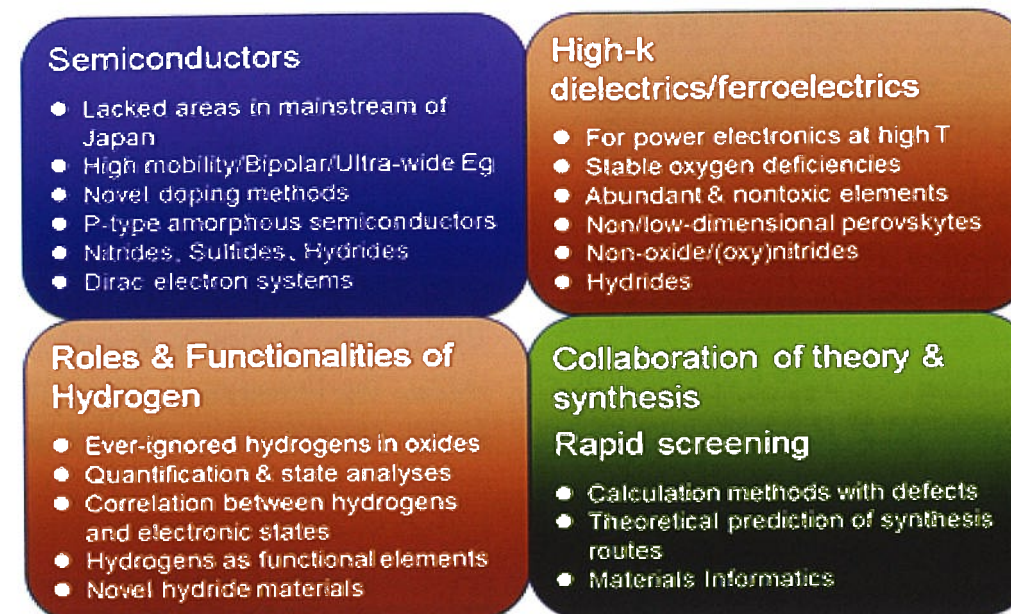


Fig. 4

JSPS Core-to-Core program

The Japan Society for the Promotion of Science (JSPS) has implemented Core-to-Core Program since 2012, which is designed to create top world-class research centers that partner over the long term with other core research institutions around the world in advancing research in leading-edge fields, on issues of high international priority. The program funds a Japanese academic research center to establish “Advanced Research Network” by forming an international and sustainable collaboration scheme with two or more foreign research centers having corresponding matching funds in each country. The fund mainly

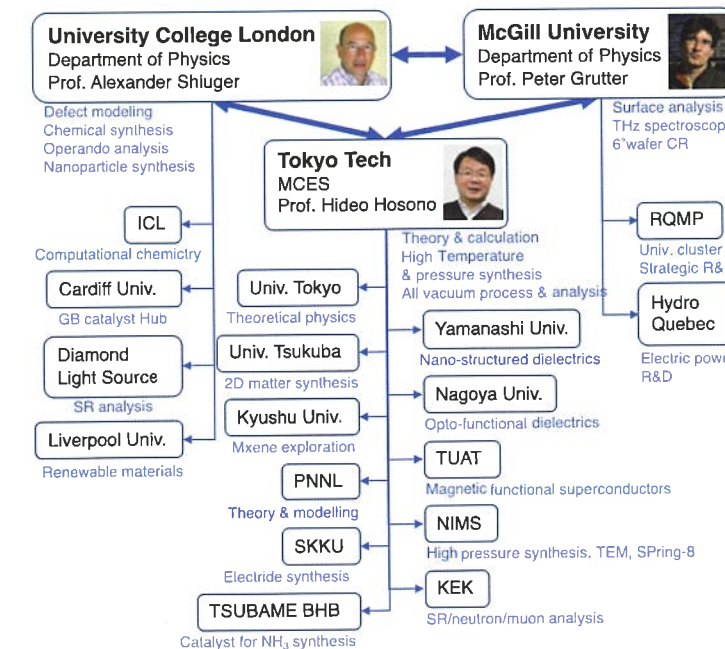


Fig. 1: International collaboration scheme under JSPS Core-to-Core Program

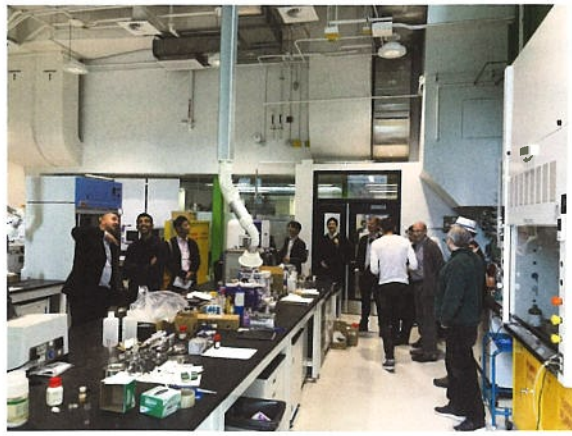


Fig. 2: Laboratory tour in the 1st workshop at McGill University.

supports collaborations among the researchers from each research center who include young researchers and students.

In 2017, MCES proposed an international collaboration scheme entitled “Defect Functionalized Sustainable Energy Materials: Design to Devices Application” to JSPS, with University College London (UCL) in United Kingdom and McGill University in Canada for four years from 2018 to 2021. The Japanese organization promoted by MCES and coordinated by Professor Hideo Hosono is comprised of MCES researchers and the domestic network based on TIES project and thus the researchers of Tokyo Tech, National Institute for Materials Science (NIMS),



Fig. 3: Brainstorming in the 2nd workshop at UCL.

High Energy Accelerator Research Organization (KEK), The University of Tokyo. The UCL and McGill University are organized by Professor Alexander Shluger and Professor Peter Grutter, respectively, and have their own domestic research networks (Figure 1). The proposal was accepted in March 2018, which was the first Core-to-Core program that was proposed by Tokyo Tech and accepted by JSPS.

The universal goal of the collaboration is to form a world-leading international collaboration institute which enable us to create innovative materials, based on new ideas demarcated from those in the previous materials research and development. Especially, we focus on sustainable energy materials such as

electronic materials for low-power consumption, high-efficiency power-generation materials, high-efficiency and power-saving catalytic materials, and so on. Ordinarily, defects in condensed matters have been regarded as origin of drawbacks of the materials. We, however, noticed that unique electronic structures formed by a part of defects could induce the origin of new functionalities of the materials. Sharing this idea as common view, the researchers of the institutes in Japan, United Kingdom, and Canada will establish novel concepts of materials design which could be a key factor to discover new functionalities and thus to derive creation of innovative energy materials, through this collaboration network. These concepts and approaches are not only consistent fully with the Element Strategy Initiative, but rather expand its scope toward the next stage of Element Strategy. Furthermore, through the active communications in the present collaboration, it is also the important goal to cultivate many of international young researchers who can take continuous creation of the innovative materials even after the present collaboration.

The research network activities started in April, 2018, which are composed of (1) workshops with oral or poster presentations of the researches, (2) laboratory tours, (3) brainstorming meetings to create

new collaborations based on (1) and (2), (4) training seminars for young researchers and students to execute collaboration researches, (5) symposia to show the achievements of the collaborations to public audiences, and (6) individual trips to collaborating research center for discussion and experiments. In May, 2018, we held the first workshop at McGill University in Montreal with 25 attendees (Figure 2). In July, 2018, we held the second workshop at UCL in London with 24 attendees (Figure 3). In November, 2018, we held the third workshop at MCES, Tokyo Tech, with 40 attendees (Figure 4). In February, 2019, we held the first symposium at UCL Wellcome Collection in London with 40 attendees (Figure 5). In May, 2019, we held the fourth workshop and the first training seminar with 50 attendees (Figure 6). As a result, 36 collaborations have been so far proposed and operating.

The research network with many collaborations under the Core-to-Core Program will continue by the end of March, 2021, and further develop even after the Program. The achievements of the Program will also promote the next stage of MCES and Element Strategy Initiative.



Fig. 4: Oral presentations in the 3rd workshop at MCES, Tokyo Tech.

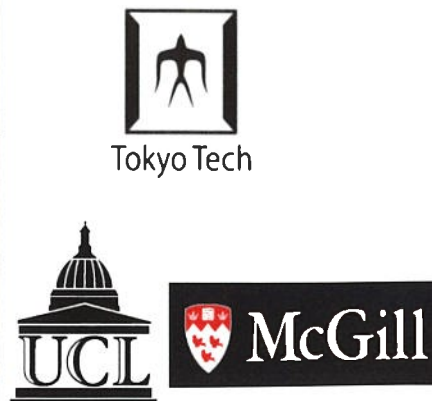


Fig. 5: The 1st symposium at UCL Wellcome Collection.



Fig. 6: Poster session in the 4th workshop at McGill University.

Pioneering on-site ammonia production: Tsubame BHB Co., Ltd.

Prof. Hosono group invented new electrone-based catalysts that differ totally from catalysts used in the Haber-Bosch process. These catalysts enable highly efficient ammonia synthesis under low-temperature and low-pressure conditions. These catalysts make it possible to produce ammonia even in small-scale plants, where production was considered difficult so far.

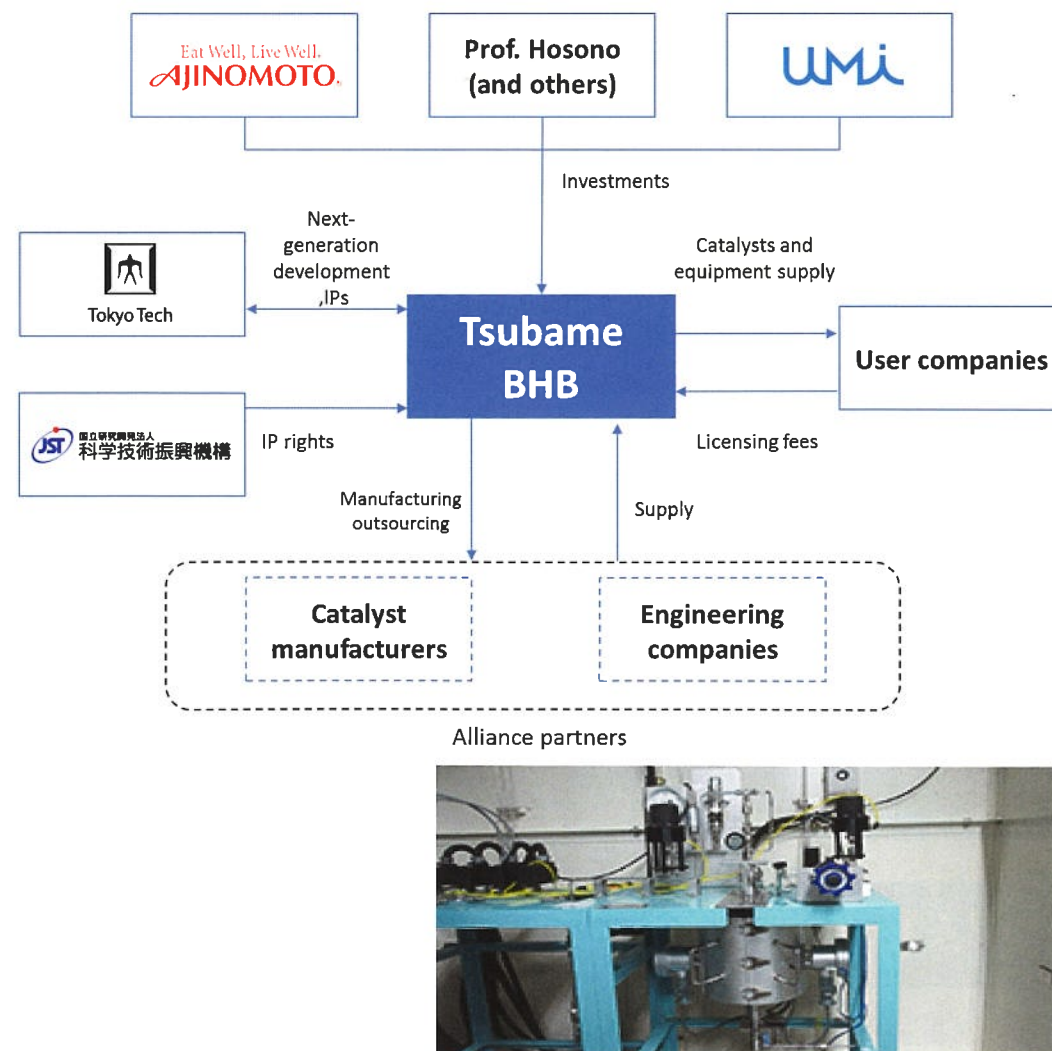
Tsubame BHB Co., Ltd. was established to develop on-site ammonia manufacturing system by Tokyo Institute of Technology professors including Professor Hosono, Ajinomoto Co., Inc. (*1) and Universal Materials Incubator Co., Ltd. (*2) on early

2017.

*1: A Japanese famous food company

*2: A venture capital which has spun out from Japanese governmental fund (INCJ)

Tsubame BHB will introduce these technologies at Ajinomoto's fermentation material plants worldwide, aiming implementation of the world's first on-site ammonia production by around 2021. In the future, in collaboration with Ajinomoto as well as a variety of partner companies, Tsubame BHB will strive to expand applications in various areas.



Research Topics

Theoretical design and development of an environmental-friendly bipolar semiconductor, Cu_3N

We developed a high-mobility bipolar semiconductor, Cu_3N (Fig. (a)), which comprises only of environmental-friendly non-toxic elements and exhibits bipolar conduction by intentional doping. Bipolar carrier doping is important to develop high-performance, high-efficiency optoelectronic devices as seen in Si and compound semiconductor devices. On the other hand, although n-type oxide semiconductor, a-In-Ga-Zn-O, is employed in commercial flat-panel displays, practical bipolar semiconductors with bandgaps appropriate for photovoltaics, ~ 1.5 eV, have not been discovered. Cu_3N was reported to be a defect-tolerant semiconductor and confirmed to exhibit n- and p-type conduction by choosing Cu-rich and N-rich growth conditions, respectively,¹⁾ but its conduction properties are not well controlled artificially.

To assess the feasibility of doping control in Cu_3N , we grew high-quality epitaxial Cu_3N (100) films on SrTiO_3 (100) single-crystal surfaces by plasma-assisted molecular beam epitaxy. We found doping is controlled by Cu/N flux rate, and p-type doping with hole densities = $10^{18} - 10^{20} \text{ cm}^{-3}$ and mobilities = $6 \times 10^{-2} - 3 \times 10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ is obtained in Cu-poor condition and n-type doping with electron densities =

$10^{19} - 10^{20} \text{ cm}^{-3}$ and mobilities = $6 \times 10^{-2} - 6 \times 10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in N-poor condition without extrinsic doping.²⁾

We succeeded in drastically improving the quality of the Cu_3N epitaxial films by nitriding Cu films with oxidized NH_3 gas.³⁾ The films exhibited an intrinsic indirect bandgap of 1.0 eV with small subgap optical absorption. Further, efficient extrinsic dopants were screened by first-principles calculations. Figure (b) shows the formation energies of interstitial dopants and predicts that halogen doping to the center vacancy site of the Cu_3N anti- ReO_3 type structure (the red sphere in Fig. (a)) have low formation energies and work as shallow acceptors in the whole range of the bandgap. Experimental confirmation was carried out by annealing polycrystalline Cu films with $\text{NH}_3 / \text{NF}_3$ mixture gases, which exhibited good p-type conduction as seen in Fig. (d) with electron and hole mobilities up to 200 and $80 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. The doping of F to the center vacancy site is confirmed by STEM-EELS measurements (Fig. (c)).

Unlike other ionic semiconductors such as ZnO, Cu_3N exhibits the high mobilities both for electrons and holes and their values are close to each other. It implies that Cu_3N is suitable for developing complementary metal-oxide-semiconductor (CMOS) devices. Actually we developed polycrystalline Cu_3N ambipolar thin-film transistors and CMOS inverters on glass, exhibiting symmetric ambipolar operations and good inverter operations with high voltage gains of ~ 100 (unpublished).

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- 2) K. Matsuzaki, T. Okazaki, Y.-S. Lee, H. Hosono, and T. Susaki, *Appl. Phys. Lett.* **105**, 222102 (2014).
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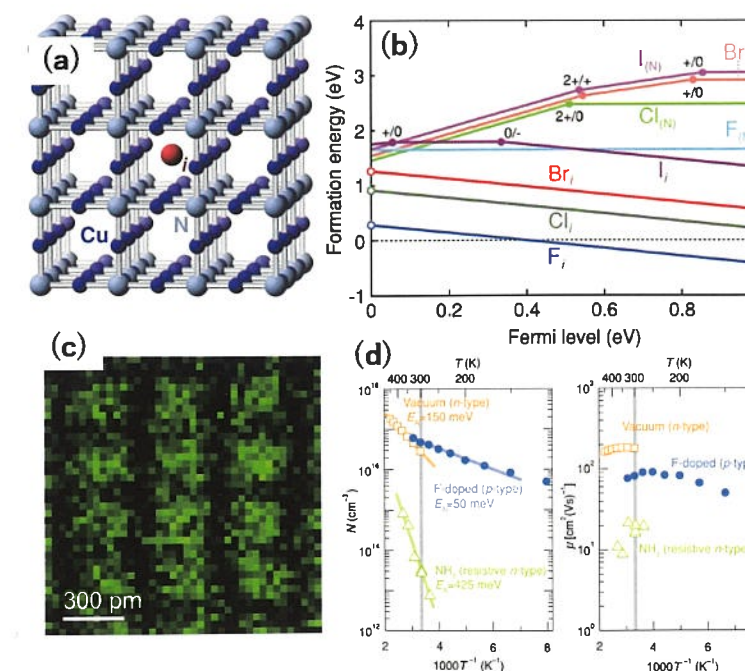


Fig. Bipolar doping in Cu_3N . (a) Structure of F_i doping, (b) confirmation of F_i doping by STEM-EELS, (c) theoretical prediction of doping, and (d) experimentally confirmed bipolar doping.

Development of highly hydrogen-sensitive thermal desorption spectroscopy system for quantitative analysis of low hydrogen concentration ($\sim 1 \times 10^{16}$ atoms/cm³) in thin-film samples

Hydrogen is the most unavoidable and uncontrollable impurity in semiconductor devices because of the ease of contamination during fabrication processes, even under an ultra-high-vacuum (UHV) atmosphere. This impurity results in serious problems such as instability of thin-film transistors and unintentional carrier doping. The detection limit of various techniques strongly depends on the sample volumes because a larger total amount of hydrogen facilitates detection. Thus, many quantitative hydrogen analyses have been performed on 'bulk' samples. However, semiconductor device technology is generally based on thin-film deposition and fine-scale processing technologies, for which material purification and refinement of processing techniques have been rapidly advancing. Thus, the development of highly sensitive hydrogen detection techniques for small-volume samples such as 'thin films' with nanometer-scale thicknesses is critical to investigate the effects of hydrogen impurities for practical semiconductor devices.

In this study, we developed a highly hydrogen-sensitive thermal desorption spectroscopy (HHS-TDS) system to detect and quantitatively analyze low hydrogen concentrations in thin films (see Fig. 1). The system was connected to an in situ sample-transfer chamber system, manipulators, and an rf magnetron sputtering chamber under an UHV atmosphere of $\sim 10^{-8}$ Pa. The following key requirements were proposed in developing the HHS-TDS: (i) a low hydrogen residual partial pressure, (ii) a low hydrogen exhaust velocity, and (iii) minimization of hydrogen thermal desorption except from the bulk region of the thin films. To satisfy these requirements, appropriate materials and components were selected, and the system was constructed to extract the maximum

performance from each component. Consequently, ~ 2000 times higher sensitivity to hydrogen than that of a commercially available UHV-TDS system was achieved. Quantitative analysis of an amorphous oxide semiconductor InGaZnO₄ (IGZO) thin film (hydrogen concentration of 4.5×10^{17} atoms/cm³, which is the minimum concentration among previously reported IGZO.) was demonstrated using the HHS-TDS system. This concentration level cannot be detected using UHV-TDS or secondary ion mass spectroscopy (SIMS) systems. The hydrogen detection limit of the HHS-TDS system was estimated to be $\sim 1 \times 10^{16}$ atoms/cm³, which implies ~ 2 orders of magnitude higher sensitivity than that of SIMS ($\sim 10^{18}$ atoms/cm³). This detection limit is the most sensitive among various conventional analysis techniques, to our knowledge, in the case of thin-film samples.

T. Hanna, H. Hiramatsu, I. Sakaguchi, and H. Hosono, *Rev. Sci. Instrum.*, 88, 053103 (2017).

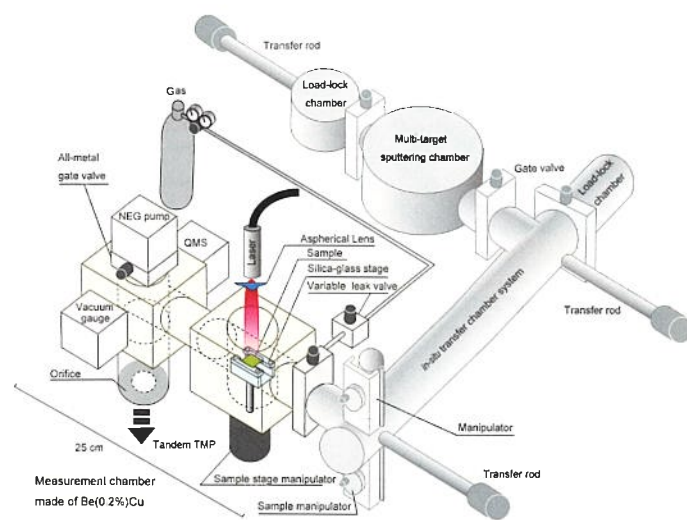


Fig. 1. Schematic illustration of the HHS-TDS system, to which an in situ transfer chamber, manipulators, and an rf magnetron sputtering deposition chamber are connected. This system is set up in the 3rd floor of S8 bldg. at Suzukake-Dai Campus of TITech.

Materials design of functional semiconductors with light emission and carrier dopabilities: ternary Perovskite sulfides $AEHfS_3$ ($AE = Sr \& Ba$)

For development of next-generation optoelectronic devices, it is strongly required to find novel semiconductors exhibiting highly efficient green-light emission together with n- and p-type conduction, because commercially available III-V group semiconductors suffer from drop of the external quantum efficiency in the green wavelength region¹). To meet the demand, we propose an original design concept based on strategies extracted from consideration on chemical bonding in solids, in which (i) the deep early-transition-metal (*eTM*, e.g., Hf, Zr) *d*- and shallow S *3p*-nonbonding states in high symmetry crystal structures form advantageous energy levels both for n- and p-type dopings²), respectively, and (ii) the direct band gap is realized by band folding stimulated by construction of the three-dimensional superstructure (e.g., distorted perovskite-type structure) from the primitive cubic structure (inset in Fig. 1), which is profitable for efficient light emission (Fig. 1). In this study, we focused on *eTM*-based distorted perovskite-type sulfides, $AEHfS_3$ ($AE =$ Alkali-earth metal) and investigated the optoelectronic functionalities³).

Polycrystalline SrHfS₃ and BaHfS₃ were synthesized via conventional solid-state reactions between AE S and HfS₂. The samples exhibited intense green and orange photoluminescence peaking at 520 and 600 nm, respectively at room temperature (RT) (Fig. 2). It should be noted that both the emissions, which are attributed to band-to-band transitions, can be seen by human eyes (insets in Fig. 2) and other emission related to donor and/or acceptor levels originating from such as defects are not detected. Additionally, both of n- and p-type conduction were successfully observed through La³⁺- and P³⁻-dopings at Sr²⁺ and S²⁻ sites in SrHfS₃, respectively (Fig. 3).

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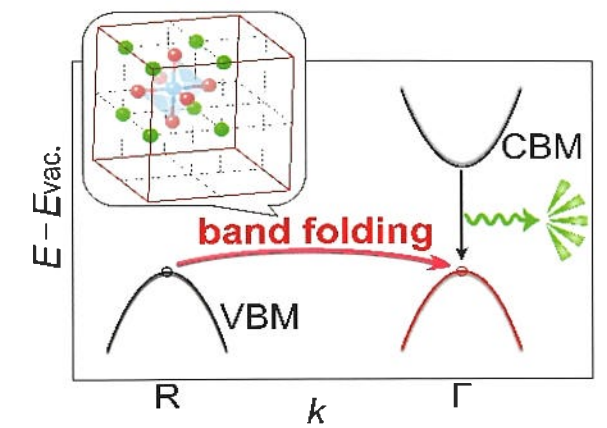


Fig. 1. Direct band gap designed using band folding from R to Γ points. Inset is an example of formation of superstructure in perovskite-type structure.

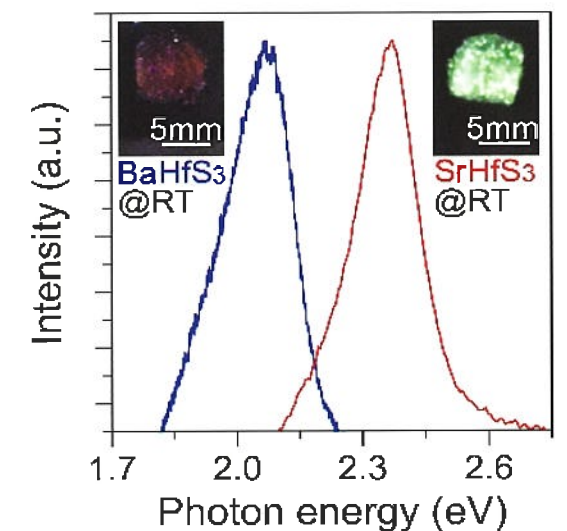


Fig. 2. Photoluminescence spectra of undoped SrHfS₃ (red) and BaHfS₃ (blue) at RT. Insets are pictures of emissions of the excited samples.

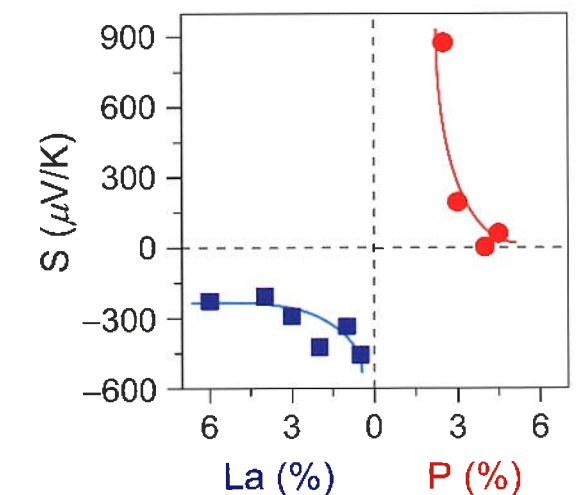


Fig. 3. Seebeck coefficients (S) of La- (blue squares) and P-doped (red circles) SrHfS₃ at RT.

Pb-free Blue-emitting 0D Cs₃Cu₂I₅ with High PLQY of ~90%

Recently, CsPbX₃ (X=Cl,Br,I) perovskite materials are promising candidates for light emitting devices and solar cells due to their excellent optoelectronic properties, and the good compatibility with the formation of thin films by low cost solution process.[1,2] However, the main component of lead (Pb) is toxic, which hinders its practical use. Furthermore, CsPbX₃ based 3D perovskite materials suffer from poor PLQY.

To resolve these issues, great efforts have been undertaken to overcome the low PLQY and toxicity of Pb. Firstly, to increase low PLQY, one of alternative approach is reducing the structural dimensionality of three dimensional (3D) materials by changing the network of metal halide to achieve quantum confinement effect. 3D halide perovskites, such as CsPbX₃, are a class of bulk materials with corner-sharing metal halide octahedra ([PbX₆]⁴⁻) that extended in all three dimensions. Owing to its small exciton binding energy (<50 meV), 3D halide perovskites readily dissociate to free carriers. On the other hands, low dimensional metal halide perovskite, such as Cs₄PbBr₆, can be regarded as core-shell quantum confined materials because metal halide is surrounded by the large Cs or large organic cation. The generated excitons are therefore confined in the metal halide site and much larger exciton binding energy (E_b) are obtained than that of 3D perovskite materials (cf. CsPbBr₃: < 50 meV, Cs₄PbBr₆: ~353 meV).[3] Based on the above idea, in this work, we choose zero dimensional Cs₃Cu₂I₅ (0D Cs₃Cu₂I₅) as a candidate material that is nontoxic, low cost, and air-stable.[4] Because we speculate that high PLQY and large exciton binding energy will be attained if their VBM primarily constitute the Cu 3d and halogen p orbital. This dispersion of hybridized orbitals is smaller than that of hybridized Pb 6s and halogen p orbital in CsPbX₃ based perovskite materials. And then, this 0D Cs₃Cu₂I₅ material consist of isolation of the photoactive metal halide [Cu-I] site by separation of Cs that inhibits interactions between the metal

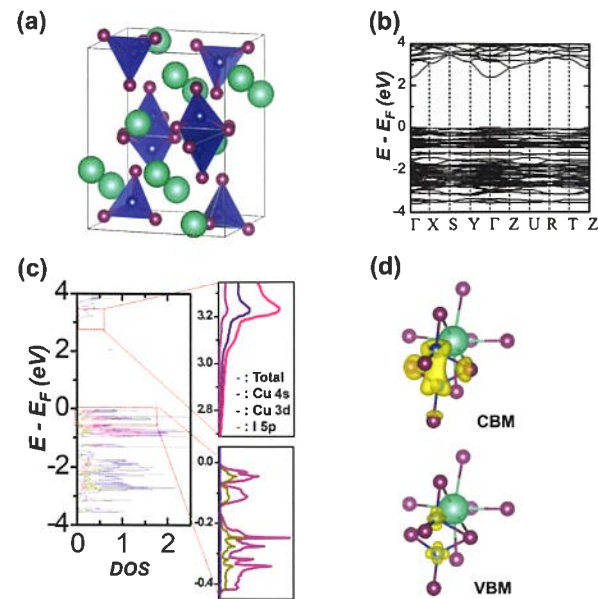


Figure 1. (a) Crystal structure of 0D Cs₃Cu₂I₅ material. (b) The projected density of states (PDOS) plots of the 0D Cs₃Cu₂I₅ material. The isosurface plots of the wave function $|\Psi|^2$ of (c) CBM and VBM. E_F: Fermi level. (d) Calculated electronic band structure of 0D Cs₃Cu₂I₅.

halide and that result in large exciton binding energy due to the confined exciton. Eventually, the 0D Cs₃Cu₂I₅ single crystal and thin film exhibited not only blue emission at ~445 nm but also high PLQY (single crystal: > 90%, thin film: > 60%).

As shown Figure 1(a), the crystal structure of 0D Cs₃Cu₂I₅ is orthorhombic in the space group *Pnma*. The crystal lattice of 0D Cs₃Cu₂I₅ consists of two types of Cu⁺ site, one of which resides in a 4-coordination site and the other Cu⁺ occupies a 3-coordination site with voids filled with Cs⁺. The individual sites of Cu⁺ tetrahedra and Cu⁺ trigonal are completely isolated from each other and surrounded by the Cs⁺ ion. To further characterize electronic properties of 0D Cs₃Cu₂I₅, we performed DFT band structure calculation. The calculated band structure for the 0D Cs₃Cu₂I₅ are shown in **Figure 1(b)**. The 0D Cs₃Cu₂I₅ has a direct bandgap at Γ point. As shown in Figure 1(c), The partial density of states (PDOS) plots show that the VBM is composed of

nearly Cu 3d orbitals, whereas the CBM is mainly derived from mixed Cu 4s and I 5p orbital. The electronic levels from Cs are located deep within the valence band and the conduction band, without contribution to the states near the Fermi level. **Figure 1(d)** shows the results of the charge distribution in CBM and VBM. It is seen in Figure 1(d) that the charge density in CBM are derived from Cu 4s + I 5p orbitals, while the charge density is concentrated at the small Cu 3d orbital in VBM state. Therefore, Cs₃Cu₂I₅ can be considered to consist of two parts: 0D photoactive site of [Cu₂I₅]³⁻ and Cs⁺ ions as the isolator.

To further verify the photophysics properties of the 0D Cs₃Cu₂I₅, we synthesize a 0D Cs₃Cu₂I₅ crystal with a size of ~ 5mm by vapor saturation of an antisolvent method. The crystal structures of 0D Cs₃Cu₂I₅ was determined using single crystal X-ray diffraction (SC-XRD), as shown **Figure 2(a)**. SC-XRD data confirmed that 0D Cs₃Cu₂I₅ crystallize in the orthorhombic space group *Pnma*. This single crystal of 0D Cs₃Cu₂I₅ also possess extremely high PLQY (~90%) at room temperature. It is worth noting that this PLQY value (~90%) is the most efficient luminescence materials developed to date. However, the PLQY for thin films will be of more interest for practical applications. Therefore, we fabricated the 0D Cs₃Cu₂I₅ thin film by a spin-coating method that is similar to the method adopted for conventional CsPbX₃ thin films. The fabricated 0D Cs₃Cu₂I₅ thin film exhibited a PLQY of ~62% at room temperature. **Figure 2(b)** shows the PLE and PL spectra of the thin film. The PLE and PL peak wavelengths are located at 290 nm and 445 nm, respectively. A large Stokes shift (~155 nm) is observed. These values are similar to these of the 0D Sn-based metal halide perovskites,

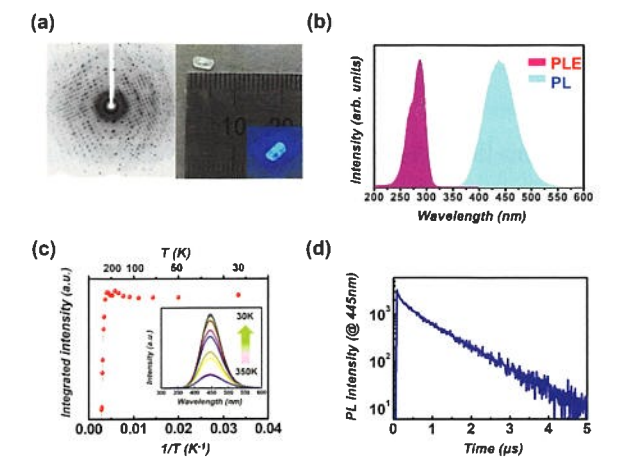


Figure 2. (a) SC-XRD and photograph of 0D Cs₃Cu₂I₅ single crystal under photoexcitation (245 nm light). (b) The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the 0D Cs₃Cu₂I₅ thin film on a glass substrate. (c) Integrated PL intensity as a function of reciprocal temperature from 30 K to 350 K. The inset of (c) shows the temperature-dependent PL spectra. (d) Time-resolved PL decay curve at room temperature.

implying that the PL mechanism cannot be explained simply by a direct band emission. Instead, the exciton self-trapping or the excited state structural reorganization is possible mechanism.

In summary, we have successfully demonstrated the novel lead free inorganic 0D Cs₃Cu₂I₅ material, as blue emission materials. 0D Cs₃Cu₂I₅ material has a high PLQY (Single crystal: ~90%, Thin film : ~60%), which is due to the unique crystal structure. Further, the solution-processability of 0D Cs₃Cu₂I₅ enabled fabrication of thin films to demonstrate a blue LED.

T. Jun, K. Sim, S. Iimura, M. Sasase, H. Kamioka, J. Kim, H. Hosono. *Advanced Materials* 30 (2018) 1804547.

New P-type Transparent Amorphous Semiconductor with High Mobility of 9 cm²/Vs

Over the last decade, thin-film transistors (TFTs) based on transparent amorphous oxide semiconductors (TAOSs) have considerably contributed to recent flat-panel display (FPD) technologies owing to their various advantages. However, it has been difficult to develop p-type TAOSs, which elucidates why the complementary circuit using TAOSs is still not realized. In fact, the reason for the difficulty in developing p-type TAOSs is easily understood from the view point of electronic structures of conventional TAOSs. The 2p-orbital of an oxygen ion is too small to have a spatial overlap with another neighboring O ion, resulting in a localized O 2p-like valence band with small hole mobility. On the contrary, metal cation's *ns*-orbital ($n > 4$) is sufficiently large to induce the large band dispersion of the conduction band. Thus, conventional TAOSs exhibit considerably high performances as n-type semiconductors. Consequently, a p-type transparent amorphous semiconductor (TAS) could be realized if large s-orbitals constitute the valence band maximum (VBM). However, it is considerably difficult to employ cation's occupied s-orbital in amorphous materials. Therefore, we propose a different material design concept for a p-type TAS in which the large p-orbital plays the role of a pseudo-extended s-orbital, similar to conventional n-type TASs. As an example, we focused on CuI because iodine (I) has a 5p-orbital, which is sufficiently large to realize the pseudo-extended s-orbital. The amorphous Cu–Sn–I (a-CuSnI) thin films were successfully fabricated using the spin-coating method. Here, Sn was employed to facilitate amorphous CuI formation. The solution was prepared by dissolving CuI and SnI₄ in 2-methoxyethanol. The electrical properties were examined via Hall effect measurements with the van der Pauw configuration, and a considerable large Hall

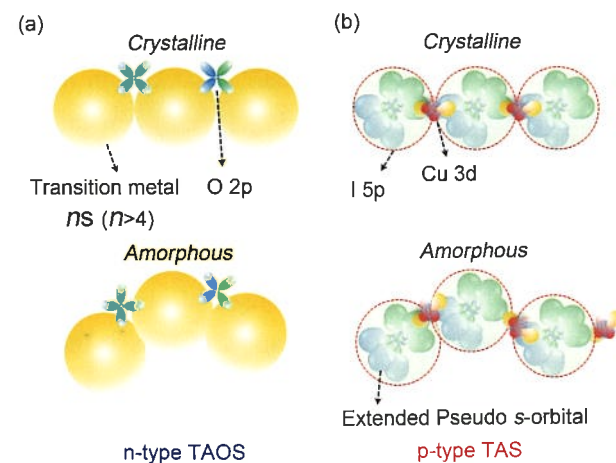


Figure 1. (a) Schematic orbital drawing of the CBM in crystalline and amorphous n-type transparent amorphous oxide semiconductors (TAOSs) based on a post-transition metal cation with an electronic configuration $(n-1)d^{10}ns^0$, where $n > 4$. (b) Schematic orbital drawing of the valence band maximum (VBM) in new p-type transparent amorphous semiconductor (TAS). Three p-orbitals with a large spatial spread may be regarded as a pseudo s-orbital similar to the 5s orbital with a large spread and a spherical shape.

mobility of $\sim 9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is comparable to that in polycrystalline CuI thin films, was obtained for a-CuSnI thin films. On the contrary, a-CuSnI thin films have a considerably smooth surface and pinhole-free morphology.

To realize p-type TASs with a large hole mobility, it is necessary to design a VBM that serves as a hole pathway using disorder-insensitive orbitals of the constituting anions. The ionic radii of these anions, which are determined by the spatial spread of the outermost p-orbitals, are large ($>200 \text{ pm}$), and their electronegativities do not significantly differ from those of post-transition metals. Since the three outermost p-orbitals of these anions are spatially spread, we may regard them as pseudo s-orbitals with large spatial spreads. The spatial spread was $>200 \text{ pm}$ in radius. This radius is larger than the radii ($\sim 180 \text{ pm}$)

of vacant 5s-orbitals of Cd^{2+} or In^{3+} , which constitute the CBM of n-type TAOS materials, e.g., a-CdO–GeO₂ and a-IGZO. Thus, we may expect to realize p-type amorphous semiconductors with a large mobility comparable to that in polycrystalline thin films using post-transition metal anions with a large spatial spread of filled p-orbitals. **Figure 1** illustrates the material design concept described above in comparison with n-type TAOS materials.

On the other hand, a strong correlation between the Hall mobility and carrier concentration was observed for the fabricated a-CuSnI thin films. Carrier concentration increased from $\sim 2 \times 10^{17} \text{ cm}^{-3}$ to $\sim 4 \times 10^{18} \text{ cm}^{-3}$ while Hall mobility increased from 3.1 cm²/Vs to 8.9 cm²/Vs. This phenomenon is quite similar to that observed for conventional TAOSs, which substantiates that the carrier transport in a-CuSnI is dominated by percolation conduction; for

crystalline semiconductors, carrier mobility decreases with the increase in carrier concentration owing to the ionized impurity scattering. On the other hand, it seems that the increase of hole concentration is attributed to the surface adsorption of a certain molecule in the ambient; the maximum Hall mobility and carrier density were obtained from the sample kept in an ambient for 2 months, while the minimum values were from the sample taken out instantly from the globe box. We also confirmed that electrical property is recovered by heat treatment (140 °C) in an inert atmosphere (Ar), which supports the possibility of surface adsorption effect. Similar behaviors resulting from O₂/OH surface adsorption have been well studied for conventional TAOSs. Consequently, a large Hall mobility of $\sim 9 \text{ cm}^2/\text{Vs}$ was obtained for a-CuSnI, which is comparable with that of polycrystalline CuI thin films.

This work demonstrated a material design concept for a p-type transparent amorphous semiconductor using copper iodide with an extended pseudo s-orbital. We believe that the design concept is applicable not only to iodides of other posttransition metals but also bromides. We expect these amorphous CuSnI materials to be applicable to transparent flexible electronics based on appropriate energy alignment with conventional optoelectronic materials and controllability of Fermi levels by postannealing, combined with excellent electrical properties and low-temperature solution processing.

T. Jun, J. Kim, M. Sasase, H. Hosono, *Advanced Materials* 30 (2018) 1706573.

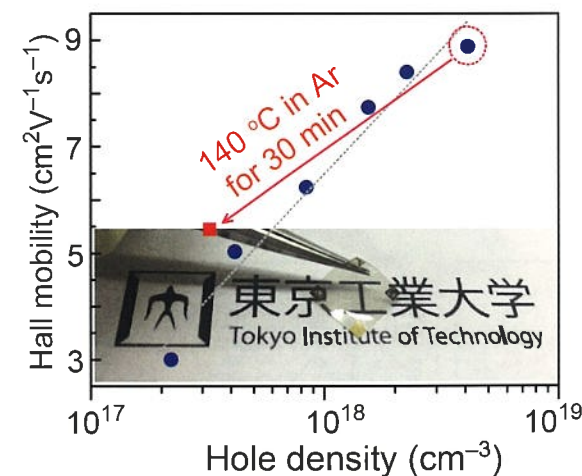
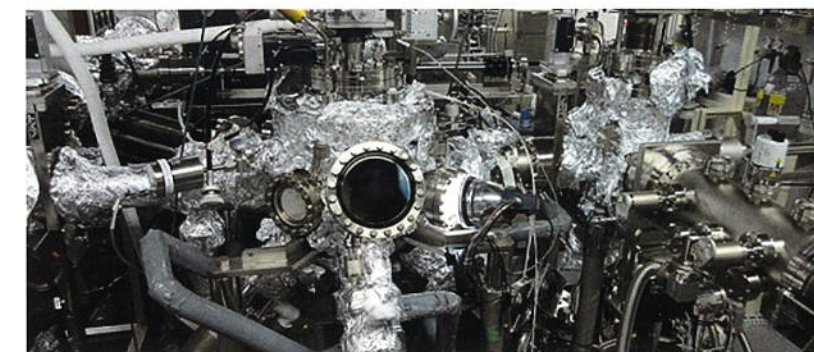


Figure 2. Dependence of the Hall mobility of a-CuSnI on the carrier concentration.



Fast hydride ion conduction in $\text{LaH}_{3-2x}\text{O}_x$ at intermediate temperature

Hydride ions (H^-) are electrochemically attractive charge carriers because of not only their small ionic radii and a valence electron shell suitable to ionic conduction in solids but also the high reduction potential of H_2/H^- (-2.23 V). In terms of the coexistence of high reaction rate and selectivity, the reduction reactions are preferred to be operated at intermediate temperature ranging 200 to 400°C. However, a lack of solid electrolyte working satisfactory at the intermediate temperature (Norby gap) has hindered the development of next generation chemical processes.²⁾

We chose a lanthanum oxyhydride ($\text{LaH}_{3-2x}\text{O}_x$) as a candidate of new H^- conductor (Fig.1a).¹⁾ La sublattice forms fcc structure and H^- occupy both the tetrahedral (T-site) and octahedral sites (O-site). The O^{2-} substitution for H^- generates a vacancy at T- and O-site through which H^- conduction progresses. At $x = 0.25$ and $T = 340^\circ\text{C}$, a high ionic conductivity over

10^{-2} Scm^{-1} was observed, which is located in the range of the Norby gap (Fig. 1b). The high conductivity is originated from a large prefactor of Arrhenius equation rather than a small activation energy (Fig. 1c). We attributed the large enhancement of prefactor at low x to the characteristics of H^- (small mass and high polarizability) and the densely packing of H^- .

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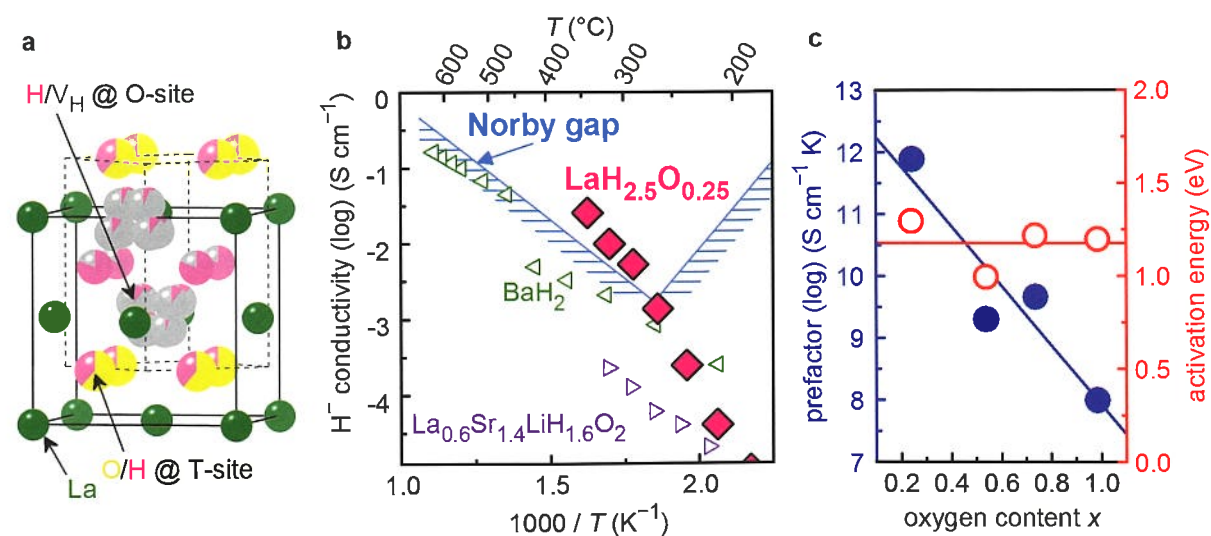


Fig.1:(a) Crystal structure of $\text{LaH}_{3-2x}\text{O}_x$. (b) Arrhenius plots of $\text{LaH}_{3-2x}\text{O}_x$ ($x = 0.25$) and H^- conductors reported to date.²⁻⁴⁾ (c) x dependence of prefactor and activation energy.

New materials exploration; New family of MAX phase

$M_{n+1}\text{AX}_n$ (MAX) phases are a class of unique materials that exhibit a combination of ceramic and metallic properties, and a mixture of covalent and metallic bonding. Therefore, MAX phases possess the features of elastically stiff, strong, and heat-tolerant ceramics, although their electrical and heat conductivities drop linearly with increasing temperature, as with a metal. For the reported MAX phases, M represents an early transition metal, A is generally a metal element in group 13 or 14, while X is limited to C or N. Utilizing the significant difference in strength between the metallic M-A bonding and covalent M-X bonding, the A-layer can be selectively etched to form two-dimensional (2D) materials known as MXenes, which cannot be synthesized directly due to their thermodynamic metastability. MAX phases and the derived MXenes thus have attracted extensive interest because of the abundance of their possible forms, structures and their broad applicability. However, the question has been raised as to whether it is possible to synthesize new MAX phases and corresponding MXene materials

without the limitation of C and N as the X.

Now we carried out the first principles evolutionary search by selecting B as X, and found a new MAX phase Ti_2InB_2 (Fig. 1(a)), a stable boron-based ternary phase in the Ti-In-B system. The predicted Ti_2InB_2 compound is successfully synthesized using a solid-state reaction route and its space group is confirmed as P-6m2 (No. 187), which is in fact a hexagonal subgroup of $\text{P6}_3/\text{mmc}$ (No. 194), the symmetry group of conventional $M_{n+1}\text{AX}_n$ phases. Moreover, a strategy for the synthesis of MXenes from $M_{n+1}\text{AX}_n$ phases is applied, and a layered boride, TiB, is obtained by the removal of the indium layer through dealloying of the parent Ti_2InB_2 at high temperature under a high vacuum. We theoretically demonstrate that the TiB single layer exhibits superior potential as an anode material for Li/Na ion batteries than conventional carbide MXenes such as Ti_3C_2 (Fig. 1(b)).

J. Wang, T.-N. Ye, Y. Gong, J. Wu, N. Miao, T. Tada, H. Hosono, *Nat. Commun.*, **10, 2284 (2019).**

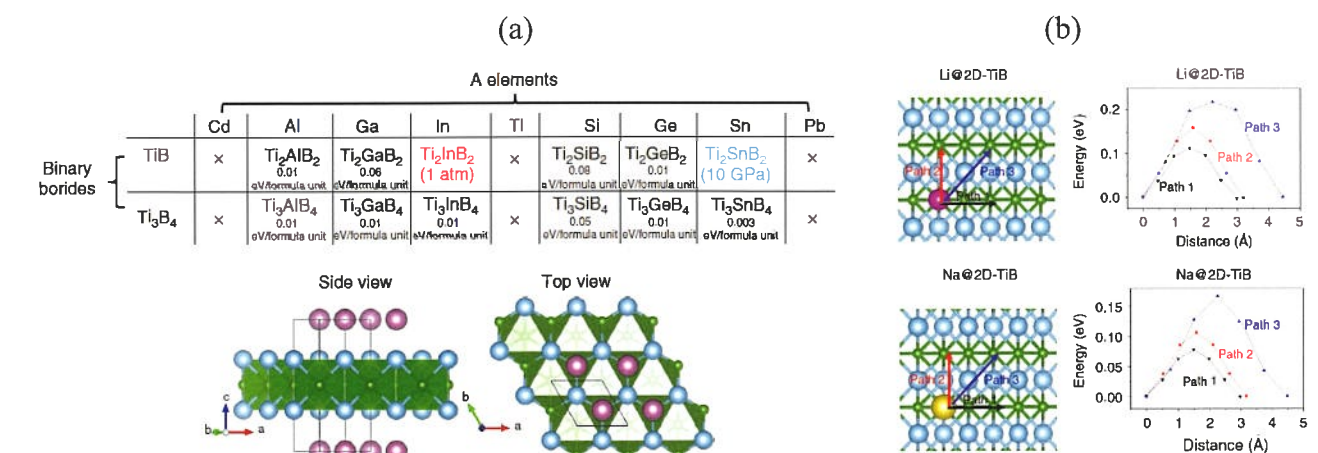


Figure 1 (a) Summary of structure search results using binary and ternary variable-composition methods, where the distances for metastable phases to the convex hull are labelled in the unit of eV per formula, and the crystal structure of Ti_2InB_2 . (b) Calculated diffusion paths for Li and Na on the TiB monolayer, and calculated diffusion energy barriers along the several migration paths. The purple and yellow atoms represent Li and Na atoms, respectively

Development of new electride-based catalysts

We have newly developed various intermetallic electride materials. These intermetallic electrides effectively promote various chemical reactions. Due to the presence of anionic electrons in the lattice, the intermetallic electrides possess various exotic properties, including low work function and reversible hydrogen absorption/desorption ability.

Y_5Si_3 is the first discovered water-stable electride¹⁾. It crystallizes in the famous Mn_5Si_3 -type structure, and accommodates periodic voids (denoted as X) which are octahedrally coordinated by yttrium atoms. Density functional calculations revealed that the site X confines anionic electrons, and its formal valence state can be written as $[Y_5Si_3]^{0.8+}:0.8e^-$. Y_5Si_3 exhibit low work function nature which is as low as 3.5 eV. Moreover, it can reversibly absorb/desorb hydrogens without largely changing its original structure. Therefore, the ammonia production rate of Ru-loaded Y_5Si_3 are as high as $1.45 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with activation energy of $52.3 \text{ kJ}\cdot\text{mol}^{-1}$ at 0.1 MPa and $340 \text{ }^\circ\text{C}$ and enhanced to $4.48 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with using Y_5Si_3 nanoparticles, demonstrating the improved catalytic activity and chemical stability. Since Y_5Si_3 is a non-oxide and non-nitride based electride, these discoveries opened the exploration of electrides in wider range of materials, particularly in intermetallic systems.

We have also developed RTX intermetallic compounds (R = rare earth, T = transition metal, X = p-block element) as new electride materials. This family of compounds shows tetragonal structure with electride features, where electrons localized inside La_4 tetrahedra serve as anions. As shown in Figure 2 by taking $LaCoSi$ ²⁾ and $LaRuSi$ ³⁾ as examples, the electronegative

lattice transition metal atoms has a strong adsorption to N_2 , making it easily to cleave $N\equiv N$ bonds by utilizing the heat released from the adsorption of N_2 (hot-atom effect).

This efficient N_2 activation is mainly

due to the electride features of RTX and the unique crystal structure which provides a favorable geometric configuration around the activation centers (Ru/Co) to trigger the catalytic activity even for the catalytic inert Co. However, the successful N_2 activation does not warrant a high activity for ammonia synthesis, because the adsorption of N is too strong. Fortunately, electride features can solve the problem. During the catalytic reactions, electron anions exchange with H anions rapidly (Figure 2), providing activated H to remove the adsorbed N efficiently by forming NH_3 . Therefore, $LaCoSi/LaRuSi$ shows one order of magnitude higher activity than conventional catalysts for ammonia synthesis. More importantly, the brand-new materials system and the mechanism derived therefrom will provide useful guidelines for the design of catalysts.

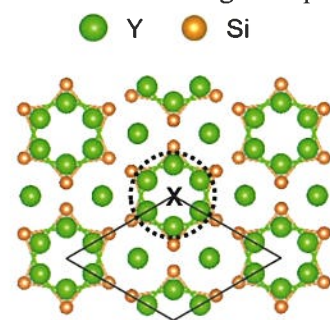


Figure 1. Crystal structure of Y_5Si_3 .

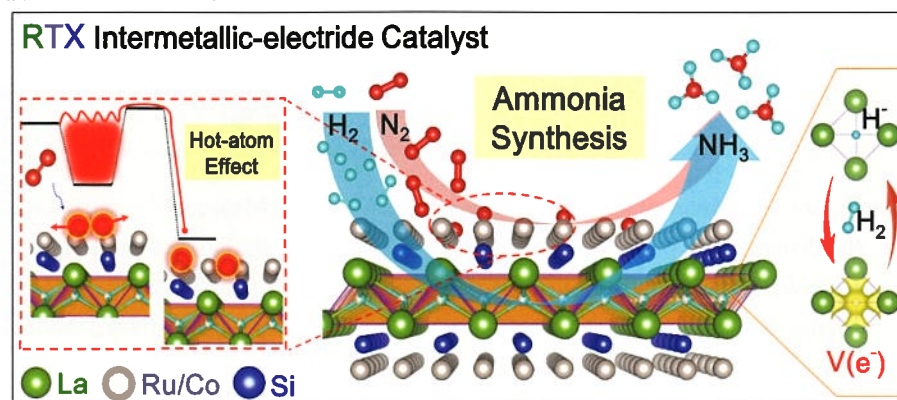


Figure 2. The schematic reaction mechanism of ammonia synthesis over RTX intermetallic electrides by emphasizing the hot-atom effect on the left side and the reversible H absorption/desorption capability of RTX on the right side.

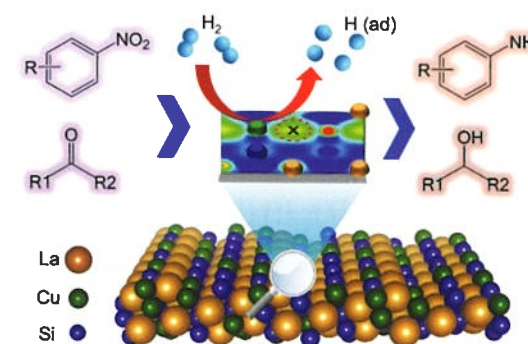


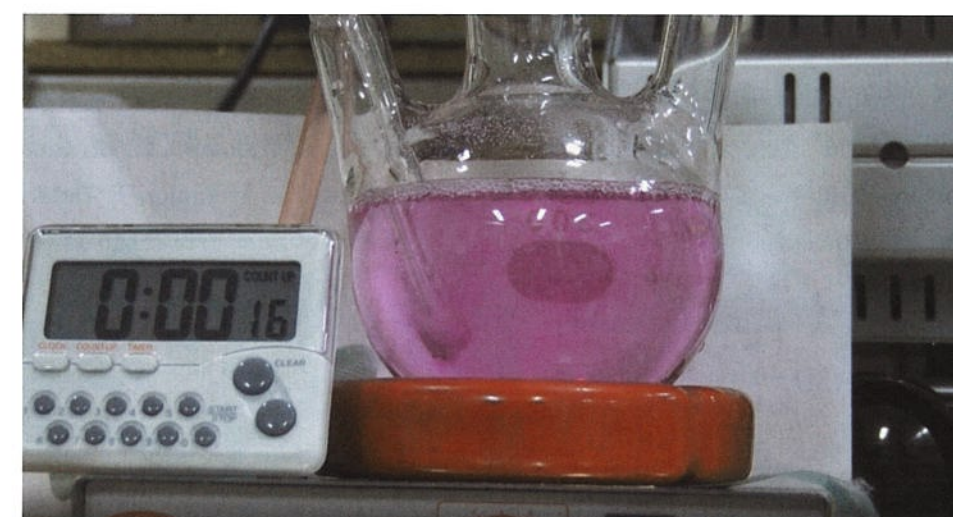
Figure 3. $LaCu_{0.67}Si_{1.33}$ for various hydrogenation reactions.

Furthermore, RTX intermetallic electrides were found to be effective for selective hydrogenation reactions⁴⁾. We have demonstrated that a new copper-based intermetallic electride catalyst, $LaCu_{0.67}Si_{1.33}$ functions as efficient catalyst for the selective hydrogenation of nitroarenes as well as carbonyl compounds. It crystallizes in a hexagonal structure, Cu and Si atoms constitute a two-dimensional honeycomb network, whereas the La layers are located between each honeycomb layer. The work function of $LaCu_{0.67}Si_{1.33}$ was measured to be 3.5 eV and the free electrons would be efficiently donated

from $LaCu_{0.67}Si_{1.33}$ to the LUMOs of H_2 (3.6 eV), which will suppress the activation energy for H_2 dissociation. Thus, $LaCu_{0.67}Si_{1.33}$ hydrogenates nitrobenzene without producing any intermediates or byproducts and the yield of aniline reaches 99% in 9 h with high TOFs of 5084 h^{-1} .

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New materials exploration; Electride

Electride is a unique material in which electrons distributed in interstitial sites can form individual orbitals and serve anions rather than being attached to atoms; we call the bare electron *anionic* electron. Electrifies were first realized in organic materials; however, their poor stabilities at room temperature and ambient atmosphere limited their potential for use in applications. In recent years, inorganic electrifies, which combine the unique characteristics of traditional organic electrifies with much improved stabilities, have received growing attention from the theoretical viewpoint and as a source of novel materials concepts. For example, C12A7 inorganic electride shows a high activity for ammonia synthesis at moderate conditions¹⁾, and therefore discovering new electride is one of the most exciting issues in Inorganic chemistry.

An evolutionary search combined with first principles electronic structure calculation is quite a powerful tool in theoretical exploration for unknown compounds. Once we provide the elements constituting target compounds, the formula and corresponding stable structures are automatically identified with the evolutionary search with the first principles method. Thus, element selection in the evolutionary search is the most critical step to discover a new compound showing a desired property. To find a new electride, we focused on the dimensions

of anionic electrons, and assumed that the stability of anionic electrons in inorganic electrifies can be represented as $0D > 1D > 2D$ (Fig. 1(a)); C12A7 and Ca_2N electrifies are respectively 0D and 2D electrifies. Based on the stability strategy, even if an unknown compound cannot be stabilized in the form of 2D electrifies, the compound has a chance to be stabilized in the forms of 1D or 0D electride. Therefore, we carried out total energy calculations for hypothetical 2D electrifies with the same crystal symmetry of Ca_2N , and identified that Sr and P can be the constituent elements for new electride in the form of 2D, 1D, and 0D. Now that we have fixed the target compounds as Sr_nP_m for new electride, we carried out the first principles evolutionary search using USPEX and VASP codes, and successfully found Sr_5P_3 1D electride (Fig. 1(b)) which was also confirmed in experimental synthesis and structural analysis with X-ray diffraction²⁾. These results indicate the powerfulness of the evolutionary search for unknown compounds.

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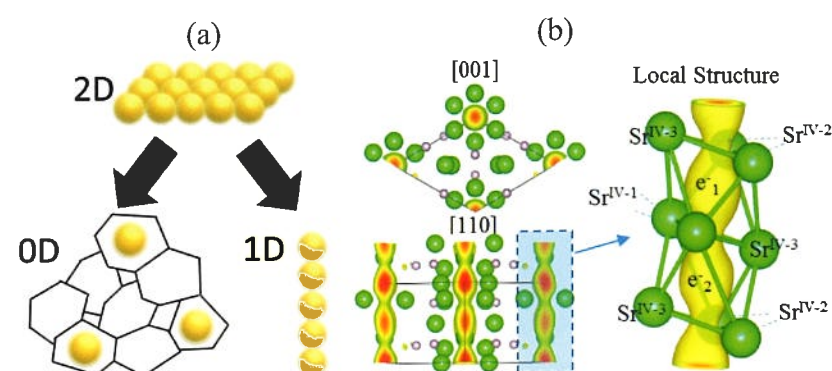


Figure 1 (a) A schematic of the dimensional strategy for finding new electrifies, and (b) discovered 1D electride, Sr_5P_3 .

Groups

Striving toward ground breaking materials based on original concept

Hideo Hosono (Institute Professor)
Soshi Imura (Assistant Professor)
Junghwan Kim (Assistant Professor)



Hosono Imura Kim

1. About us

A material is a substance that is intended to be used for real applications. Our laboratory has developed new materials based on our own design concepts (Fig.1). Our research goal is to cultivate new frontier in materials science and to lead to distinctly contribute to the social issues through our research achievement. What we emphasize is to create original design

2. Research interests

2-1. Transparent amorphous transistor

In 1997, we reported a first time p-type transparent oxide semiconductor, CuAlO_2 , which opens up a new research field, *oxide electronics* (*Nature* (1997)). Subsequently, we realized a high performance thin film transistor (TFT) using crystalline (Science 2003) and amorphous oxide semiconductor In-Ga-Zn-O (so called IGZO) (*Nature* (2004)). These TFTs have been applied to drive liquid

concept for functional materials. Research activity of our group covers from computation, synthesis, property evaluation, characterization and proto-type device fabrication.

We are extensively doing a cooperative research with academia and industry.

crystal displays, such as those mounted on smartphones and tablets. Now, it is also used to drive large-sized OLED televisions.

IGZO is designed to realize a high electron mobility even in amorphous materials that is comparable to that of polycrystalline thin films. We focused on post transition metal oxides with ionic bonding nature. In this material series, the bottom of

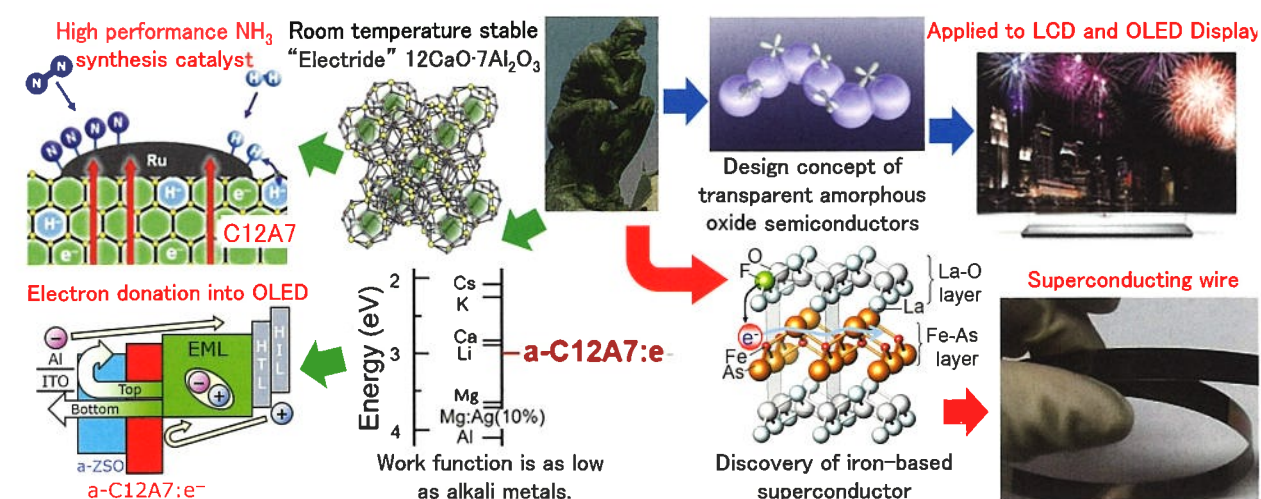


Fig.1: Function cultivation based on our own materials design concept.

the conduction band is made up mainly of 3D-percolated metal s-orbitals with a large spatial spread. The large overlap of these metal s-orbitals enables electrons to move easily even in amorphous materials.

2-2. New concept material: Electride

Electride is a unique material in which electrons act as anions. $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C12A7) consists of CaO and Al_2O_3 , both of which are ubiquitous and typical insulators. What we focused is the characteristic crystal structure composed of positively charged cages encapsulating O^{2-} . By employing various chemical/physical treatments, these O^{2-} ions can be replaced with various anions such as H^- , F^- , Au^- and “electrons” (*Nature* (2002), *Science* (2003)). The C12A7 electride (C12A7:e^-) is metal rather than insulator, and shows superconductivity at low temperature. By choosing a positively charged layer and tunnel structures, a 2-dimensional and 1-dimensional electrified are also formed (*Nature* (2013), *JACS* (2014)).

Due to the loose binding of electrons in the cage, the

2-3. Element strategy

If new functional materials consisting only of ubiquitous elements could be developed, it should provide significant advantages. Recently, we newly developed amorphous Zn-Si-O (a-ZSO) that works pretty well as an electron transport layer (ETL) for perovskite electroluminescent devices (PeLEDs). a-

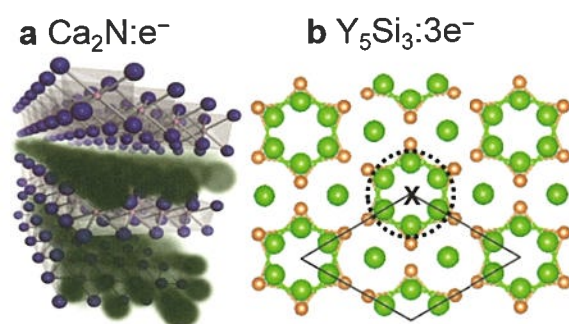


Fig. 2: Example of crystal structures of 2D (a) and 1D electride (b)

In 2018, we extended this concept to p-type amorphous materials, Cu-Sn-I, in which the hole conduction progresses through a large 5p orbital of I (*Adv. Mater.* (2018)).

C12A7:e^- possesses a work function as low as that of alkali metals but chemically inert. By utilizing the intrinsic nature of electride, we applied C12A7:e^- to the catalyst of ammonia synthesis and found that C12A7:e^- accelerates the formation of ammonia by donating electrons into a high energy antibonding state of nitrogen adsorbed on Ru nano particles loaded on the surface of C12A7:e^- (*Nat. Chem.* (2012)). Recently, we extended the concept of electride from ionic compounds to intermetallics and are exploring new catalyst that can activate high-energy multiple bonds without using rare metals (*Nat. Catal.* (2018)). The nature of low work function of C12A7:e^- is also useful as an electron injection layer of OLED, since organic emission layers usually have a shallow LUMO (*PNAS* (2017)).

ZSO possesses a high electron mobility of $1 \text{ cm}^2/\text{Vs}$ and a small electron affinity of $\sim 3.2 \text{ eV}$. It was revealed that a-ZSO significantly enhances electron injection efficiency and exciton confinement effect. These features achieved a quite high performance PeLEDs. The PeLED exhibits a very low operating voltage (2.9 V at $10,000 \text{ cd/m}^2$) and ultra high brightness of $500,000 \text{ cd/m}^2$ at 5 V. (*Appl. Phys. Rev.* (2019)).

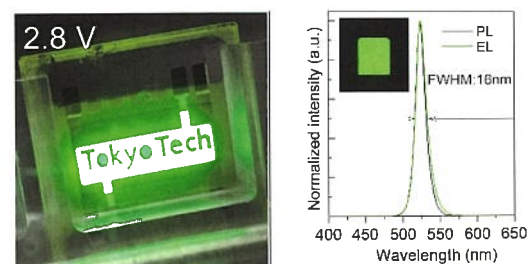


Fig. 3: Green PeLED with a-ZSO ETL.

Materials research utilizing hydride and metal element anions

Satoru Matsuishi (Associate Professor)



The properties of ionic solid materials largely depend on the electronic states of metal cations such as transition and rare-earth metal ions. However, we explore the novel property of materials taking advantage of “unusual anions”. Hydride ion H^- is an anion of hydrogen which is not commonplace in oxide unlike proton H^+ . By partial replacement of O^{2-} by H^- , heavy electron doping is achieved in oxide-based materials ($\text{O}^{2-} \leftrightarrow \text{H}^- + e^-$). By applying this technique for the parent of iron-based superconductor LaFeAsO , we discovered the new superconducting phase in the heavily electron-doped region cannot be accessed by F^- -substitution. [1] The H^- -substitution is also applied for the tuning of emission wavelength of rare-earth-activated phosphors. We succeed in the full substitution of H^- to F^- in $\text{Sr}_2\text{LiSiO}_4\text{F}$ known as phosphor host for Eu^{2+} . [2] By substituting H^- to F^- in the coordination sphere around Eu^{2+} , excitation and emission bands of the $4f \leftrightarrow 5d$ transition are redshifted. Then, $\text{Sr}_2\text{LiSiO}_4\text{H:Eu}^{2+}$ becomes the intense yellow emitting phosphor can be excited by violet LED chip (Fig. 1). Heavy metal elements with large electronegativity such as Au can form anionic states in the compounds with alkali- an alkaline-earth metals. Ca_3PbO ($\text{Ca}^{2+}_3 \text{Pb}^{4-}\text{O}^{2-}$) is the anti-perovskite-type crystal with Pb^{4-4-} ($6p^6$) state and its Dirac semimetallic state with Pb 6p and Ca 3d bands was theoretically predicted. By using angle-resolved photoelectron spectroscopy and Shubnikov-de Haas oscillations measurement, we demonstrated the Dirac semimetallic state based on anionic state of

heavy metal element Pb. Substitution and insertion of hydride or metal anion will be key techniques to convert ubiquitous element compounds to novel electronic materials.

- [1] S. Iimura, S. Matsuishi, H. Sato, T. Hanna, Y. Muraba, S-W. Kim, J-E. Kim, M. Takata and H. Hosono, *Nat. Commun.* **3**, 943 (2013).
- [2] T. Wu, A. Ishikawa, T. Honda, H. Tamatsukuri, K. Ikeda, T. Otomo and S. Matsuishi, *RSC Advances* **10**, 5282-5287 (2019).
- [3] Y. Obata, R. Yukawa, K. Horiba, K. Kumigashira, Y. Toda, S. Matsuishi and H. Hosono, *Phys. Rev. B.* **96**, 155109 (2017).
- [4] Y. Obata, Y. Kohama, S. Matsuishi, and H. Hosono, *Phys. Rev. B.* **99**, 115133 (2019).

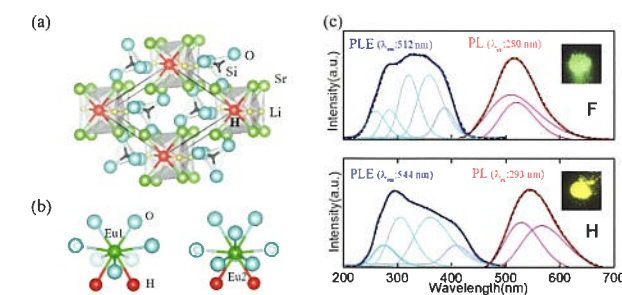


Figure 1. (a) Crystal structure of $\text{Sr}_2\text{LiSiO}_4\text{H}$. (b) Coordinate Structures around Eu^{2+} . (c) Photoluminescence emission and excitation spectra of $\text{Sr}_2\text{LiSiO}_4\text{F:Eu}^{2+}$ (upper) and $\text{Sr}_2\text{LiSiO}_4\text{H:Eu}^{2+}$ (lower).

Electride and hydride materials for catalytic ammonia synthesis

Masaaki Kitano (Associate Professor)

Nitrogen activation to form ammonia (NH_3) is a key technology for supporting human life because NH_3 is used as a source for the production of synthetic fertilizers, nitric acid, and nitrogen-containing chemicals. Owing to the strength of the $\text{N}\equiv\text{N}$ bond, industrial NH_3 synthesis (Haber–Bosch process) must be conducted using promoted iron-based catalysts at high reaction temperatures (400–500°C) and high pressures (10–30 MPa). Low temperatures are thermodynamically favorable for high NH_3 production, and small-scale NH_3 synthesis processes are now in demand for on-site ammonia production.

Recently, we have developed various electride and hydride-based catalysts for low temperature ammonia synthesis. $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride (C12A7:e^-) with low work function (2.4 eV) functions as an efficient electron donor for a Ru catalyst in ammonia synthesis (**Nature Chem.** 2012). Furthermore, hydride ions (H^- ions) are formed in the cages of C12A7:e^- and reversible reaction between H^- ions and anionic electrons occurs at the Ru–support interface during NH_3 synthesis. This smooth anion exchangeability suppresses H_2 poisoning on the Ru surface. These unique properties of electride shifts the bottleneck in ammonia synthesis (**Nature Commun.** 2015). Not only electrides but also hydride materials such as Ca_2NH and CaH_2 promote the activity of Ru catalysts significantly at low reaction temperatures and with low activation energies (50–60 kJmol^{-1}) when these materials are used as catalyst supports (**Chem Sci.** 2016) (Figure 1).

Very recently, we have demonstrated that Barium-doped calcium amide ($\text{Ba-Ca}(\text{NH}_2)_2$) enhances the efficacy of ammonia synthesis mediated by Ru and Co by 2 orders of magnitude more than that of a conventional Ru catalyst at temperatures below 300°C (**Angew. Chem. Int. Ed.** 2018). Furthermore, the

presented catalysts are superior to the industrial Fe catalyst. Nanosized Ru–Ba core–shell structures are self-organized on the $\text{Ba-Ca}(\text{NH}_2)_2$ support during H_2 pretreatment, and the support material is simultaneously converted into a mesoporous structure with a high surface area ($>100 \text{ m}^2\text{g}^{-1}$). During the reaction, $\text{Ca}(\text{NH}_2)_2$ is converted into Ca_2NH at the metal–support interface. These self-organized nanostructures account for the high catalytic performance in low-temperature ammonia synthesis (Figure 2).

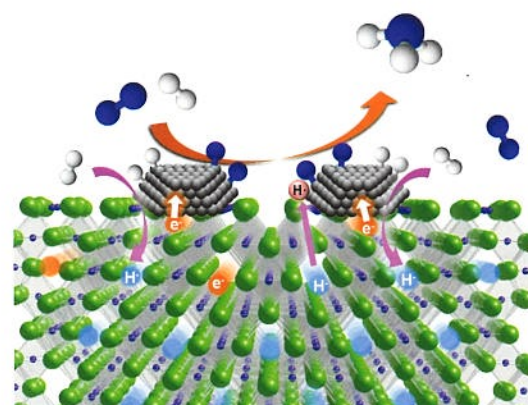


Figure 1. Schematic illustration of ammonia synthesis over Ru/ Ca_2NH .

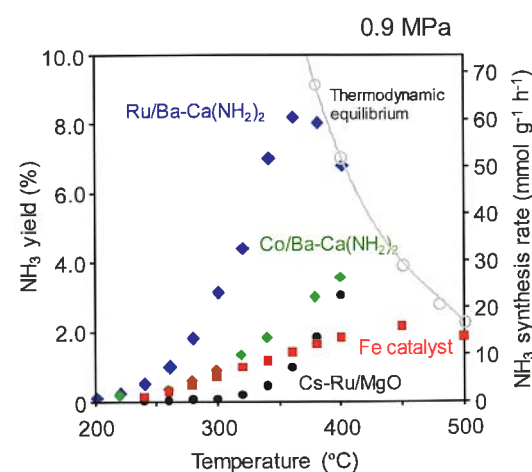


Figure 2. Ammonia synthesis over $\text{Ba-Ca}(\text{NH}_2)_2$ based catalysts.

Computational materials designing

Tomofumi Tada (Associate Professor)



About Research Purpose

Recently, computers and computational algorithms has been developed rapidly, and computational materials designing has grown up as a fundamental research tool in the field of materials science. In particular, first-principles electronic structure method is one of the most reliable computational tool for both known and unknown materials, because the first-principles method does not require any experimental parameters in principle. In addition, state-of-the-art algorithms such as Monte Carlo sampling, genetic algorithm, neural network, etc, have been extending

Research Topics

Materials design #1: New materials: *electride*, hydride, MAX phase, etc.

Materials design #2: Fast ionic conductors: oxide, hydride, etc.

Materials design #3: Catalysis: *electride*, hydride, oxide, etc.

Materials design #4: Molecular electronics: a single

Research equipment

Xeon multi-core processors

GPU accelerator

TSUBAME super computer system

Imagination

Messages

Materials computation would give you many possibilities. When you are interested in our laboratory, please visit my room. Let's share fruitful time with us.

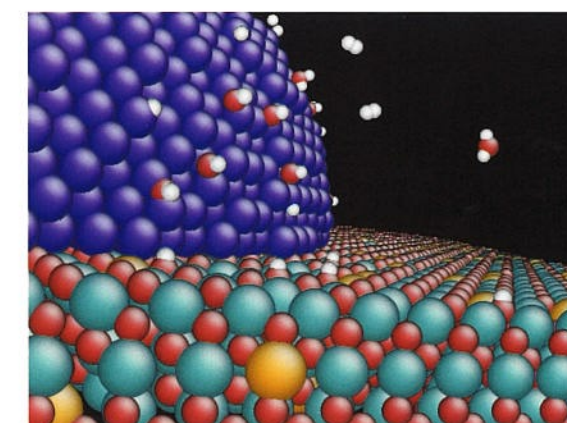
the searching area of materials and size-and-time domains of dynamics in materials. In this laboratory, we are working on new materials designing using the state-of-the-art algorithms with first-principles method, and developing computational algorithms (including *quantum* algorithms) for future computational materials designing.

molecule for diode, spin-filter, quantum-bit, etc.

Algorithm development: #1: Kinetic Monte Carlo for ionic diffusion/chemical reaction, etc.

Algorithm development: #2: Non-equilibrium Green's function for electron tunneling.

Algorithm development: #3: *Quantum* algorithm for future computations



$$H\Psi = E\Psi$$

Floor Guide

5F: Synthesis of Materials
(Furnaces, Glove boxes, Floating Zone Melting, SPS)



4F: Material Characterization and Catalytic Chemistry
(Spectroscopy (IR, Raman, vis-UV, ESR, Ellipsometer, ESR), XRD, PPMS, SQUID-VSR)
(Evaluation system for chemical reaction)



3F: Synthesis and Characterization of Thin Film
(PLD, Sputtering, MBE, ARPES, XRD, AFM, XRF)

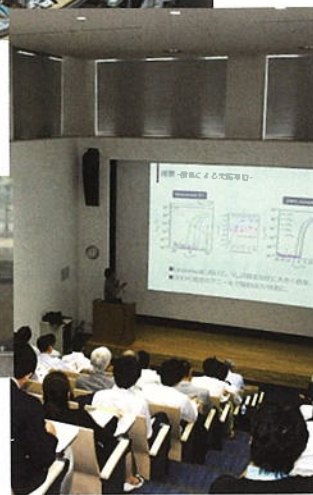
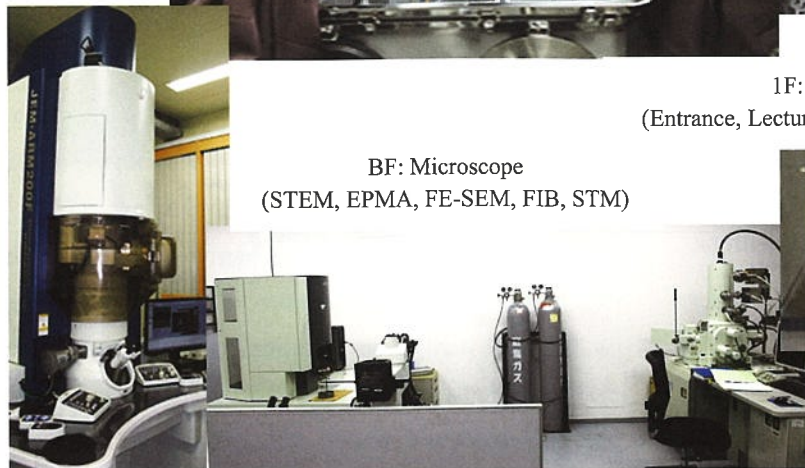


2F: Collaboration with Industry for Catalysis and Display



1F: Amenity Space
(Entrance, Lecture hall, Lounge)

BF: Microscope
(STEM, EPMA, FE-SEM, FIB, STM)





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