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ABSTRACT BOOK

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Scalable Nanomechanical Computing

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Nanomechanical computers promise robust, low energy information pro- cessing. However, to date, electronics have generally been required to interconnect gates, while no scalable, purely nanomechanical approach to computing has been achieved. Here, we demonstrate a nanomechanical logic gate in a scalable architecture. Our gate uses the bistability of a nonlinear mechanical resonator to define logical states. These states are efficiently coupled into and out of the gate via nanomechanical waveguides, which provide the mechanical equivalent of electrical wires. Crucially, the input and output states share the same spatiotemporal characteristics, so that the output of one gate can serve as the input for the next. Our architecture is CMOS compatible, while realistic miniaturisation could allow both gigahertz frequencies and an energy cost that approaches the fundamental Landauer limit. Together this presents a pathway towards large-scale nanomechanical computers, as well as neuromorphic networks able to simulate computationally hard problems and interacting many-body systems.

Computational Platform for Designing High-functional Nanocatalysts via AI-Machine Learning and First-principles Calculations

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Nanocatalysts are at the central position to promote various chemical. Innovative design of highly functional catalyst materials has been, however, delayed. In molecular level computational electrochemistry new research paradigm has been established, which substantially incorporates IT-based artificial intelligence (AI) technology into machine learning algorism. Using the new computational methodology high-throughput screening of promising nanoparticle candidates has been attempted for various desired applications. Whether the frontier approach is successful or not is significantly controlled by the reliability and accuracy of input database. It is true that substantial amounts of the data are come by previous literatures and often ab-initio calculations with idealized model systems. The conditions in which the data were generated may be so different from the operando circumstances of the target materials. To secure extreme-level integrity of the database the in-situ measurement of nanoparticle structures should be carried out, from which the reliable correlation of the structure-performance-design principle can be identified. Using first-principles calculations we studied nanoparticles with adsorbate ligands in liquid solution to establish three-dimensional (3D) structure and property database, which are, then, analyzed through AI-based neural-network approach with high speed and accuracy. The

information includes sizes, lattice distortions, and defects with picometer resolution under nonvacuum conditions. The computational outcomes are rigorously validated from the 3D liquid-cell electron microscopy. The approach is indeed 'knowledge-based' AI, which can be expected to make groundbreaking ways toward the quantum nanoarchitecture for hybrid interface materials. **(Up to 500 words)**

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Two-dimensional Material Design for Electronic Applications

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The development of electronics based on carbon nanomaterials is of interest in both academia and industry. However, the widespread application of carbon-based electronics is still restricted by considerable technical challenges. For example, graphene is considered a promising material for high-speed transistors due to its high carrier mobility of more than 2×10^5 cm² V⁻¹ s⁻¹ at low temperatures, but it is not suitable as a channel material for FETs because it has no bandgap. Designing carbon-based materials with suitable bandgaps, air stability, and high mobility to is a daunting and promising task for the development of carbon-based nanoelectronics.

In this talk, we present several theoretical designs of carbon-based two-dimensional (2D) materials suitable for electronic applications. One of them is 2D carbon nitrides (CNs). First-principles calculations combined with the local particle-swarm optimization (PSO) algorithm method were applied to explore stable structures of 2D CNs with various C/N ratios ($C_{1:x}N_x$).¹ It is predicted that $C_{1:x}N_x$ structures with low N-doping concentration contain both graphitic- and pyridinic-N based on their calculated formation energies, while pyridinic-N is predominant in $C_{1:x}N_x$ with N concentration larger than 0.25. Additionally, $C_{1:x}N_x$ structures with low N-doping concentration are more energetically favorable. The theoretical calculations are in good agreement with experimental observations that the fabricated nitrogen doped graphene always has low N concentrations and a mixture of N dopants. Moreover, we found that the restrictions of mixed doping and low N concentration can be circumvented by using different C and N feedstocks, and by growing NG at lower temperatures.

Another carbon-based material we designed is 2D C_2P_4 material.² The 2D nanomaterial C_2P_4 consists of five-membered rings of carbon and phosphorus atoms. It is both mechanically and thermodynamically stable. Besides, it has both positive (0.34) and negative Poisson's ratios (-0.11) in the characteristic direction and can sustain tensile strain up to 20%. Moreover, the maximum electron and hole mobility of C_2P_4 is 1913 cm²V⁻¹s⁻¹ and 460 cm²V⁻¹s⁻¹ by using DPT at room temperature. These excellent properties provide C_2P_4 with promising applications in nanoscale electronic devices, high-temperature electronics, flexible nanodevices, and sandwich panels for aircraft or automobiles etc.

Particularly, among the explored 2D $C_{1,x}N_x$ structures, we found that C_3N has a medium band gap (~ 1.2 eV) and can be experimentally synthesized. Our theoretical study found that significant bandgap engineering of bilayer C_3N is achieved in our work by controlling the stacking order or applying an external electric field.³ Compared with monolayer C_3N , the bandgaps of C_3N bilayers stacked with AA' and AB' are reduced, and the C_3N bilayer with AA' stacking has a much larger bandgap reduction than that of the bilayer structure with AB' stacking, apparently due to the greater overlap of the pz orbitals between the layers. Moreover, under an electric field of ~1.4 V nm-1, a bandgap reduction of nearly 0.6 eV in the AB' structure was predicted by calculations and further confirmed by experimental observations. This effective bandgap engineering of 2D-bilayer C_3N offers a new opportunity for high performance carbon-based electronics.

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Interface Design for Stable Lithium Metal Anode

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Lithium metal anodes has been placed great expectations on as a promising anode candidate for next-generation energy storage systems, such as such as lithium–sulfur, lithium–air, solid state batteries. However, the unstable interfaces between lithium anode and electrolyte definitely induce the undesired and uncontrollable growth of lithium dendrites, which results in the stable hazards and limited cyclic life of the rechargeable batteries.

Several strategies have been proposed herein towards the construction of interface for dendritefree and stable lithium metal anode. First, in-situ chemical/electrochemical reactions has been applied to built on lithium meal anode a stable solid electrolyte interphase (SEI). Both the chemical compositions of the SEI and their spatial distributions have shown tremendous influence on the stability of lithium metal interface. On the other hand, artificial interface design based on polymer matrix have been explore as well. The general idea is to utilize both the properties of rigid inorganic components and the soft organic components, and realize the rational design of functional composite interface for lithium metal anodes. The composite electrolyte interface with tunable mechanical properties and enhanced lithium ion transportation properties benefit the uniform plating of lithium metal anodes.

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The Lithium Bonds in Lithium Batteries

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As one of the most important applications of the element, Li batteries afford emerging opportunities for the exploration of Li bond chemistry. In this talk, the historical development and concept of the Li bond are reviewed, in addition to the application of Li bonds in Li batteries. In this way, a comprehensive understanding of the Li bond in Li batteries and an outlook on its future developments is presented. The Li bond was described in the context of Li batteries, including discussions of sulfur cathodes, liquid electrolytes, and Li metal anodes. Such discourse on the chemistry of the Li bond can provide fruitful insight into the fundamental interactions within Li batteries and thus deliver a deeper understanding of their working mechanism. Nevertheless, further investigations are necessary for a comprehensive understanding of Li bond chemistry, including its clear designation, geometrical and electronic structures, features that differ from other bonds involving Li, and their typical functions in Li batteries.

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Preparation of Janus-type Surface-modified Niobate Nanosheets

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Abstract: Inorganic nanosheets have attracted enormous attention, and they are typically prepared from layered materials via exfoliation. Since interlayer surfaces of some layered metal oxides undergo grafting reactions, it is possible to prepare metal oxide nanosheets where functional groups and polymer chains are immobilized via robust bonds. Among inorganic nanosheets, Janustype inorganic nanosheets have been developed in recent years.[1] It is possible to prepare Janustype inorganic nanosheets via regioselective grafting reactions at interlayers and subsequent exfoliation, and the unique structure and interlayer surface reactivity of potassium hexaniobate, $K_{A}Nb_{c}O_{17} \bullet 3H_{2}O$, which consists of niobate layers, $[Nb_{c}O_{17}]^{4-}$, and interlayer potassium cations, are very attractive for regioselective grafting reactions: two different interlayers with different reactivities for ion exchange reactions, highly reactive interlayer I with hydrated potassium cations and anhydrous interlayer II with potassium cations exhibiting low reactivity, appear alternately in the stacking direction of niobate layers. It is known that intercalation compounds which contain guest species only at interlayer I can be obtained via regioselective ion-exchange reactions with bulky organoammonium.[2] Since expansion of interlayers by ion-exchange reactions with organoammonium ions is required for grafting reactions in interlayers, surface modification at interlayer I can regioselectively proceed by using these intercalation compounds and phosphoruscontaining coupling agents.[3] By exfoliating this type of organic derivatives at both interlayers I and II, Janus-type nanosheets where one of two surfaces is modified can be prepared. When initiator groups for atom transfer radical polymerization were immobilized at interlayer I and thermoresponsive polymer chains were grown at interlayer I, the resultant nanosheets were dual functional; one function was ion-exchange capability of unmodified surface and the other one was thermoresponsiveness. [4] It is also possible to modify interlayer II of organic derivatives with grafted interlayer I by introducing smaller organoammonium ions and subsequent grafting reactions at interlayer II.[5] Exfoliation at both interlayers I and II leads to the formation of Janus nanosheets, and individual nanosheets possess two different groups separately on two sides. By selecting appropriate immobilized groups, water-dispersible Janus-type nanosheets, which can stabilize an o/w emulsion, were prepared, indicating that they acted as a two-dimensional surfactant.[6]

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Polymorphism Engineering for Energy Conversion

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Abstract: Manipulating the arrangement of atoms as building blocks enable human beings to construct materials/crystals with targeted properties as they are designed, where one stoichiometry can have several different crystalline phases, i.e. so-called crystalline polymorphism. However, with atomic order degree reduced, the crystalline materials will become amorphous due to the long-range order broken. Diverse atomic arrangements can readily form multiple amorphous solids/phases, i.e. so-called amorphous polymorphism. On the other hand, the dimension of a crystal can be reduced from bulk, to nano, and even to atomic scale in one or multiple directions, which change materials properties dramatically. All these polymorphism and size related features play critical roles in various applications, e.g. photovoltaics, optoelectronics, and catalysis. In this talk, two kinds of functional condensed/solid materials will be discussed. The first one will be photo-sensitive two-dimensional (2D) materials for photocatalysis and the second one is metallic 2D materials for electrocatalysis.

Hydrogen as a clean fuel has always been attracting researchers' intense interest. This talk will discuss the materials preparation, their properties and their activities in heterogeneous catalysis. First, the research on the development of new photocatalysts for photoredox reactions based ammonia storable H₂ fuel production will be presented and discussed based on transition metal sulfides/oxysulfides. Our research outcomes indicated the crystalline/amorphous polymorphism and light-responsivity can play the critical roles in designing and developing the efficient photocatalysts for nitrogen fixation. Second, transition metal dichalcogenides (TMDs) are known to possess several different (2H, 1T, 1T') phases. To pursue the highly electrical conductivity and active catalysis, the 1T'-TMDs are especially welcome. However, the synthesis of large-area single layer TMDs using colloidal strategy is still challenging. This talk will share our recently developed general bottom-up synthesis method under mild conditions to prepare 1T'-TMDs monolayers. Our results showed that the crystalline polymorphism and tensile strain play the critical roles in the active and stable electrocatalytic hydrogen production.

In short, nanomaterials with rich engineerable parameters, including polymorphism, energy gap, and strain, provide promising avenues to tailor materials structures, enhance functionalities and extend the performance stability for nanoenergy. The explored co-relationships between structuring, reactivity and stability are expected to shed light on the further development of next-generation nanoenergy technologies. This would make a corresponding contribution to reducing the gap between scientific studies and industrial applications. This talk highlights the synergistic materials science and engineering can provide the opportunities to customize nanomaterials for advanced modern technology development.

MOFs and Composites for CO, Cycloaddition Reactions

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^aDepartment of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan, ^bDepartment of Chemistry, National Chung Hsing University, Taichung 402, Taiwan ^cDepartment of Chemistry, Chinese Culture University, Taipei 111, Taiwan There is an urgent need to convert CO₂ into useful chemical products, which can significantly improve the environment and promote sustainable development. Over the past several decades, metal-organic frameworks (MOFs) have shown outstanding gas adsorption ability and heterogeneous catalytic activity due in part to their high internal surface area and chemical functionalities.¹ Our recently studies show that the green-synthesized MIL-47 and MIL-101(Cr) and microporous 2D In-MOFs have been tested for their catalytic ability in chemical fixation of CO₂ gas through the conversion of CO₂ and epoxides to the corresponding cyclic carbonates which shows promising results to use them as catalysts.^{2,3} We also reported a SiO₂@MOF coreshell microsphere for environmentally friendly applications. The validly optimized MOF-coated SiO₂-based core-shell was successfully synthesized and characterized. The SiO₂@MOFs displayed catalytic activity on the chemical fixation of CO₂ with epoxides.⁴

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Transport of Nanofluids with Applications

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High Performance of Ceramics and Manufacturing Process Innovation

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A new competitive funding program of "High Performance of Ceramics and Manufacturing Process Innovation" supported by Japan Science and Technology Agency (JST) was completed in 2021, which had been ongoing since 2016. This program is the "Industry needs response type" in A-STEP (Adaptable and Seamless Technology Transfer Program through Target-driven R&D) aiming to bolster Japanese industrial competitiveness by contributing to the solution of technical issues common in industry. The sale in fine ceramics production in Japan is almost 40 % in the world and the ceramics family is expected to be expanded all over the world. To improve the fine ceramics industry from basic science side, the "High Performance of Ceramics and Manufacturing Process Innovation" has been selected as one of A-STEP program.

NIMS project of "Fabrication of highly structure-controlled ceramics through advanced fine powder processing" has been conducted for over 10 years and related to the projects in A-STEP program. In this presentation, at first some researches on the innovative ceramic manufacturing processing in A-STEP program will be introduced [1]. Through the process innovation based

on basic science, it is expected to establish a generic technology and the breakthrough of the manufacturing process. Then some achievements in ceramic processing at NIMS such as colloidal processing under external field will be shown. The controlled development of texture is one of the ways for effectively improving properties of ceramics. We have demonstrated a new processing of textured ceramics with a feeble magnetic susceptibility by colloidal processing in a high magnetic field and subsequent sintering. To obtain the oriented materials with feeble magnetic susceptibilities, the following conditions are necessary: well-dispersed single crystal suspension, non-cubic crystal structure, larger magnetic energy than thermal motion energy. This processing can be applied to fabricate many kinds of textured ceramics with non-cubic structure, such as Al₂O₂, AlN, Si₂N₄, MAX phase ceramics, (Zr,Hf)B₂, B₄C, etc. [2]. Next topics is the electric current activated/assisted sintering called as SPS [3]. The SPS method was successfully applied to electric conductive ceramics such as WC-diamond, (Zr,Hf)B₂-systems, MAX phase ceramics, semiconductors such as B4C compounds, and low electrical conductive ceramics such as transparent alumina, CNT-alumina nanocomposites. Recently SPS furnace is used to Flash-Sinter (FS) conductive powders, such as ZrO₂, SiC, ZrB₂, etc. The FS-SPS is interesting both in basic phenomena and industrial application [4].

For the development of high-performance ceramics, feedback from advanced analytical technology, computer science, and simulations is crucial. JST works to accelerate innovative driven by close collaboration among industry, academia and government, and facilitated by a platform for dialogue among all three sections.

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Electrocatalytic Performance of the Strontium Selenide Nanowires as pH-Dependent for Hydrogen Evolution Reaction

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Incredible Attempts have been devoted directed to develop a consistent electrocatalyst structure for hydrogen evolution reaction, but challenges are still pending. The efforts have been limited to transition metal compounds due to their boosting characteristics. Alkali and alkaline metals including post-transition elements based compounds reveal rich surface chemistry and exhibit good electrochemical characteristics for energy storage and conversion devices. Such compounds need attention to explore and adopt some strategies to resolve the existing problems. Herein, the alkaline metal-based electrocatalyst, strontium selenide nanowires with various contents of strontium have been synthesized successfully using the hydrothermal process at 200 °C for 24 hours. The strontium selenide nanowires (Sr_2Se_1) with 2 times greater contents of the strontium exhibited a good HER activity. HER activity has been evaluated by varying the pH of the Dulbecco's Phosphate Buffered solution using the 1 M KOH and electrolyte, using 2 M KOH and 0.2 M H_2SO_4 . Sr_2Se_1 nanowires attained a good current density at higher pH values and exhibited an overpotential of 130 mV at pH of 13.10, with an onset potential of 0.362 $V_{Ag/AgCl}$. Sr_2Se_1 nanowires have also exhibited a good Tafel slope of 58 mVdec⁻¹ at pH 13.30, and followed the Volmer-Heyrovsky phenomena. Sr_2Se_1 nanowires also revealed a greater turnover frequency of 211.50 ms⁻¹ at the fixed reversible hydrogen electrode potential of 1.0 V. Efficient HER activity of the Sr_2Se_1 nanowires may be attributed due to a greater electrochemical and specific surface area, suitable strontium contents and better intercalation of the electrocatalyst cations and electrolyte ions at the specified pH value. The symmetric system, consisting of Sr_2Se_1 nanowires, has also revealed a good Tafel slope of 84 mVdec⁻¹ and followed the Volmer-Heyrovsky phenomena. The results indicated that Sr_2Se_1 nanowires exhibit good HER activity and can be employed as a suitable electrocatalyst.

Direct Air Capture at Room Temperature of Sodium Manganates

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 CO_2 absorption properties from air under various relative humidity conditions at room temperature of the synthesized $Na_{0.66}MnO_2$ with a layered structure were investigated. XRD, TG-DTA, FTIR, and gas chromatography revealed that $Na_{0.66}MnO_2$ absorbed CO_2 and H_2O at room temperature to produce sodium carbonates and a layered manganate phase which is a different layered structure from $Na_{0.66}MnO_2$. The synthesized $Na_{0.66}MnO_2$ showed a large CO_2 absorption rate at room temperature when the relative humidity was increased. $Na_{0.66}MnO_2$ was reproduced when the CO_2 -absorbed $Na_{0.66}MnO_2$ was heated at 150 °C.

Session: JST-ERATO Special Session: Yamauchi Materials Space-Tectonics Project (Broadcasted from the JST-ERATO Center Venue)

Acceleration of an Electrophilic Reaction Driven by the Polar Surface of Two-Dimensional Aluminosilicate Nanosheets

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To increase chemical reaction rates, general solutions include increasing reactant concentrations to increase collisions, raising the temperature to overcome the activation energy of the reactants, and using catalysts to decrease the activation energy. Contrary to this, in this study, a rate constant enhancement for electrophilic metal coordination reactions was observed not by the abovementioned general solutions but by a surface of layered aluminosilicate (LAS). To investigate this reaction, H₂TMAP and H₂TMAP-LAS were mixed with zinc(II) chloride in a specific molar ratio in water at various temperatures. The reaction rates in each case were determined from time-dependent absorption spectra. Furthermore, Arrhenius plot was drawn from these data. In addition, the causes of the differences in the rates are discussed based on data from solid-state

NMR, XPS, and theoretical calculations. Thus, the rate constant was found to have increased 23fold on the LAS surface. It was also revealed that the values of activation energy remained similar regardless of the presence of LAS, and the frequency factor increased significantly when H₂TMAP was adsorbed on the LAS surface. Therefore, the higher re-action rate was attributable to the higher frequency factor on the surface. This was an unexpected consequence because the frequency factor was expected to decrease owing to one side of the molecule being obscured by the surface, preventing the approach of the metal ions. This is a remarkable example demonstrating that even chemically inert materials such as LASs have the potential to accelerate chemical reactions. Although the acceleration of the reaction by controlling activation energies has been widely studied using catalysis, controlling the frequency factors without increasing the concentration has not been well explored. Thus, this approach would be a new strategy to improve the reaction rates of chemical reactions such as organic synthesis. We anticipate the same effect for other inorganic anionic surfaces, such as niobium or titanium salts, or even metal oxides with polar surfaces. For photochemical device fabrication, the reported method may be applicable in one-pot syntheses of organic–inorganic hybrid complexes such as artificial photosynthetic systems.

Metal-Organic Framework Derivatives for Promoted Capacitive Deionization: From Oxygen-Free to Oxygenated Saline Water

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Capacitive deionization is an electrochemical desalination technique based on electrosorption or faradic reactions on materials-water interface. The interface interaction between electrode materials and saline water is a key process in CDI and is the focus of growing attention in water sustainability and environmental electrochemistry. Significant effort in the past has been mainly directed to developing porous carbon materials for promoting the salt adsorption capacity and cycling stability. Unfortunately, CDI with these materials are often performed in oxygen-free saline water, which complicates quantitative evaluation of CDI performance towards practical use and thereby impedes progress in this field. More recently, evidence has pointed out that carbon materials usually experience serious performance degradation especially when saline water contains dissolved oxygen, which is recognized as simulative natural saline water environment for CDI operation. In this lecture, I will discuss the significance of metal-organic framework (MOF) derivatives including carbonaceous and MOF hybrid materials to replace the predominance of typical carbon materials, especially for CDI of oxygenated saline water. In particular, the synthetic strategies to expand MOF derivatives will be discussed based on our former publications in this field. Through carefully comparing the published data regarding CDI performance (salt adsorption capacity versus cycling lifetime) of MOF derivatives with typical carbons, it is expected that MOF derivatives with promoted CDI performance even in oxygenated saline water would be the future choice for industrial CDI application

Functional Upcycling" of Polymer Waste Towards the Design of New Materials

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The diversification of polymer waste recycling is one of the solutions to improve the current environmental situation. Among others, upcycling is a promising strategy to convert polymer waste to chemical feedstock and high-value products. While catalytic transformations into small molecules are actively discussed, upcycling into new materials has not been actively addressed yet. Recently, the surface functionalization of polymer wastes (polyethylene terephthalate bottles, polypropylene surgical masks, rubber tires, etc.) and their conversion into new materials with enhanced functionality was proposed as an appealing alternative for dealing with polymer waste recycling / treatment. We demonstrated the possibility to upcycle polyethylene terephthalate (PET) bottles to the advanced adsorbents [1,2], separator of organic molecules and catalyst [3]. Our strategy includes the hydrolysis of PET surface for the release of terephthalic acid (TA) and its derivatives for the insitu growth of porous metal-organic framework (MOF) of the surface of PET. Alternatively, we could upcycle another common polymer polypropylene (PP) by deposition another type of MOF. Simple deposition of the superhydrophobic fluorine-free metal-azolate framework (MAF-6) leads to the preparation of advanced materials PP-MAF6 for oil spill cleanup. Importantly, the specific performance of upcycled materials is often within or higher level compared to the similar materials prepared from the virgin feedstock. All these advantages make functional upcycling a promising diversification approach to the common polymer waste postprocessing methods.

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Measurements of Chiroptical Properties and Development of Chiral Sensors

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The consideration of linear birefringence (LB) and linear dichroism (LD) in the measurement of optical rotation (OR) and circular dichroism (CD) in anisotropic crystals is very important. As OR, optical activity (OA) is observed for chiral substance, while Faraday rotation (FR) is observed for magneto-optical substance. LB and LD are optical anisotropies that denote the difference in refractive indices and absorptions, respectively, between two orthogonally polarized lights in an anisotropic crystal. Schellman et al. reported that LB and LD signals are usually 10³–10⁵ times larger in magnitude than OR and CD signals. Therefore, the accurate separation of OR and CD from LB and LD is a challenge. Furthermore, Shindo et al. pointed out that optical elements, devices, and detectors installed in polarization modulation spectroscopy cause serious systematic errors and non-negligible artifacts. This critical issue has been widely recognized in the field of chiral science. Many research groups have developed optical measurement theories and polarimeters to overcome this issue. Eventually, OR and CD in the anisotropic condensed matter were successfully measured. In particular, our group developed a novel optical apparatus called the generalized-high accuracy universal polarimeter (G-HAUP), which simultaneously measures the wavelength dependences of the OR, CD, LB, and LD in an anisotropic medium [1]. In this presentation, OR (OA or FR) measurements of chiral benzil crystals and magneto-optical CeF crystals and so on with the G-HAUP will be presented [2-5].

In addition, we are now developing chiral sensors based on mesoporous Au film as a JST-ERATO Yamauchi Materials Space-Tectonics Project. We will also briefly present the recent progress related to the project.

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Ferroelectric and Piezoelectric Properties in Single Crystal and Nanoporous Thin Film

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In the field of conductive, dielectric, and magnetic materials, the development of stable functional materials is strongly required. Especially, it is difficult to design dielectric crystals which can control electric polarization unlike the conductive and magnetic materials. The fusion of different components has potential to create new possibilities. The introduction of impurity in the dielectric materials has shown great improvement. Ferroelectric Triglycine sulfate (TGS) family is used for infrared sensors due to its high pyroelectricity. The polling processes are needed to obtain high pyroelectric performance, because the preferred orientation of electric polarization before their use is significant. We have found the preferred orientation, which means the single domain structure in alanine-doped TGS (ATGS) crystals. Furthermore, it was found that the direction of the preferred orientation of the electric polarization was opposite depending on the chirality of alanine [1]. We succeeded in determining the absolute polarity

in TGS crystals. We have suggested the mechanism of preferred polarity [2]. The creation of porous structure in the dielectric materials has also shown great improvement. Ferroelectric barium titanate (BaTiO₃; BTO) family is one of the environmentally friendly lead-free piezoelectric materials to replace lead zirconate and lead titanate, Pb(Zr,Ti)O3 (PZT). Especially, Ba_{0.85}Ca_{0.15}(Ti_{0.9} Zr_{0.1})O₃ (BCZT) film has

attracted attention as a promising piezoelectric material. However, the value of d_{\parallel} and k_{\parallel} in BTO is still far behind that of its commercially available Pb-based counterparts [3]. We have found the giant d_{\parallel} in nanoporous BCZT film. Comparing to non-doped BTO, non-porous BCZT and PZT, the value of d_{\parallel} for nanoporous BCZT is much larger than that for them [4].

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Synthesis of Hydroxide Hollow Nanoparticles by Using Water-soluble Selfsacrificing Templates

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Hollow nanoparticles are very unique materials, because they possess high specific surface area and high diffusion property due to nanoparticle and hollow morphology, respectively.1 Therefore, hollow nanoparticles can be applied as an attractive catalyst with high reactive sites and high mass transport. However, the synthesis method is not generalized, and some of the compounds cannot be obtained with hollow nanoparticle morphology. Metal hydroxides including cobalt, iron, and nickel atoms have been focused as an alternative electrocatalyst of noble metals for oxygen evolution2 and reduction3 reactions, because Co, Fe, and Ni are much cheaper than noble metals. However, their catalytic activities are not enough for practical application, and should be further improved. Therefore, we focus on hydroxide hollow nanoparticles for improvement of catalytic activity, although such compounds have not been obtained by conventional synthesis method. In this presentation, I propose the new synthesis method for hollow hydroxide nanoparticles by using metal fluorides with perovskite structure (KMF3: M = Co, Fe) as a water-soluble sacrificing template. Because KMF3 is dissolved in water, KMF3 nanoparticles can work as an easily removal template for hollow nanoparticles. Therefore, the new synthesis route is composed of two steps: (i) conversion of KMF3 surfaces into M(OH)2 and (ii) dissolution of unreacted KMF3 inside the particles. Here, I show the cases of KCoF3 and KCo4/5Fe1/5F3 for formation of Co(OH)2 and Co and Fe-included layered double hydroxide (CoFe-LDH), respectively. (i) Formation of Co(OH)2 from KCoF3 KCoF3 obtained solvothermally was dispersed in ethanol, and treated with NaOH or KOH aqueous solution. The obtained samples possessed core-shell structures, and the structure in the case of KOH aqueous solution was clearer than that in the case of NaOH aqueous solution. Further treatment with water for dissolution of unreacted KCoF3 led to the formation of hollow nanoparticles. The hollow nanoparticles were composed of α - and β - Co(OH)2 phases, indicating the successful synthesis of Co(OH)2 nanoparticles. Also, the difference of the alkaline solution led to the guality of the structure, and the case of KOH agueous solution caused clearer hollow nanoparticle structures. The difference in the structural quality between the cases of NaOH and KOH can be explained by the difference in the solubility of the byproducts (NaF and KF, respectively). NaF with smaller solubility should prevent from the crystal growth of Co(OH)2 on the surface of KMF3 to lead to the formation of Co(OH)2 degraded hollow structure after the dissolution of unreacted KCoF3 and NaF by water treatment. (ii) Formation of CoFe-LDH from KCo4/5Fe1/5F3

In the case of KCo4/5Fe1/5F3, the hollow nanoparticles were also obtained through treatments with KOH aqueous solution and subsequently with water. The morphological conversion behavior was the same as that in the case of KCoF3. Judging from the XRD patterns, the hollow nanoparticles possessed CoFe-LDH phase. Probably, Fe2+ atoms were oxidized to Fe3+ during the treatment with alkaline solution to form CoFe-LDH.

In conclusion, Co(OH)2 and CoFe-LDH hollow nanoparticles were obtained by using KCoF3 and KCo4/5Fe1/5F3, respectively, as a water-soluble sacrificing template. This method can be used for formation of the other metal hydroxide hollow nanoparticles.

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