

Joint Symposia

The 9th Advanced Functional Materials & Devices & The 4th Symposium for Collaborative Research on Energy Science and Technology

Online

March 4 (Fri) - March 5 (Sat), 2022



LETTER OF INVITATION

Dear Distinguished Professors, Researchers, and Students

On behalf of the Organizing Committee for the 9th Advanced Functional Materials & Devices (AFMD) and 4th Symposium for Collaborative Research on Energy Science and Technology (SCREST), we cordially invite you to attend the symposia and participate as **the Invited speaker** in the scientific programs **from March 4 to 5, 2022**. The symposia attempt to share the latest innovations, advances, and future multidisciplinary research and development of functional materials with a primary focus on the connection between fundamental science, engineering applications, and commercialization of the materials.

The participants and organizers will benefit a lot from your expertise on the topic. We are looking forward to meeting you via online!

I look forward to hearing from you.

Sincerely yours,

Mitsunobu Sato, Symposia Chairperson
KUTE, Tokyo

Call for Paper

The joint symposia of the 9th **Advanced Functional Materials & Devices (AFMD)** and 4th **Symposium for Collaborative Research on Energy Science and Technology (SCREST)** will be held online from March 4 to 5, 2022! The International Advisory and Organizing Committees cordially invite you to attend the symposia and participate in their scientific programs. The symposia will be held not only for members of FMS (Functional Materials Society), NUS (National University of Singapore), and KUTE (Kogakuin University of Technology), but also for non-members introduced by the above members.

Functional materials that are different from traditional structural materials have received a dramatic increase in their demands in research, development, and applications. Various novel materials with different functions have recently been developed and discovered, and some of them have successfully been used in some applications.

The symposia aim to assess the current status and to identify future priorities and directions in researches, design, and applications of different advanced functional materials including but not limited to ferroelectric and ferromagnetic materials, magneto-optical materials, thermoelectric materials, shape-memory materials, fuel-cell, and battery materials, and other related advanced functional materials.

The symposia attempt to share in the latest innovations, advances, and future multidisciplinary research and development of functional materials with a primary focus on the connection between fundamental science, engineering applications, and commercialization of the materials. The symposia also provides an opportunity for promoting mutual interaction, information dissemination, and exchange, fruitful collaborations on advanced state-of-the-art functional materials research and development. Due to the rapid growth in research and development (R&D) of functional materials in recent years, various advanced and multifunctional devices have been developed and manufactured, which stimulates a wave of design of new devices that fully use the functionality of different types of functional materials.

Conference Venue: The symposia will be held online.

Language: English will be the official language during the symposia.

Author's Guidelines

The main theme of Joint symposia: Advanced Technologies for SDGs

Topics for submission include, but are not limited to:

- Bulk from nano – Lego building
- Coordination of molecules
- Energy storage materials for the new century
- Functional thin film materials
- Futuristic organic and inorganic materials for photoluminescence and applications
- Hybrid materials for multitasking systems
- Ion liquid and ionic materials
- Lead-free oxides for piezoelectric, ferroelectric, and pyroelectric applications
- Materials and devices with multifunctionality
- New materials and systems for energy storage and harvesting
- Memory materials
- Modelling and simulation of functional materials
- Modern and advanced characterizations

Registration

There is no registration fee for all participants! Please register at the following URL.

<https://forms.office.com/r/Y851cKH56s>

Submission

Method of submission

We accept abstracts for only oral presentations. Abstracts should be prepared according to the abstract template. The abstract should be sent via e-mail (afmd@sc.kogakuin.ac.jp). The deadline for abstract submission would be **February 21, 2022**. The authors are encouraged to submit a camera-ready abstract (A4-size with 25 mm margins on all sides) in Word or PDF format. Use Times New Roman font. In the PDF file case, all fonts should be embedded in the file. The abstract should be completed within 1 page.

We welcome the submission the full paper to

Functional Materials Letters; <https://www.worldscientific.com/worldscinet/fml>

Materials (Special Issue "Synthesis and Characterization of Superionic Conductive Glass and Ceramics", The submission fee will be Discounted!);

https://www.mdpi.com/journal/materials/special_issues/superionic_conductive_glass_ceramics

Important deadlines

Abstract submission: 21 February 2022

Deadline for registration of presenters: 21 February 2022

Notification of acceptance: 25 February 2022

Deadline for registration of audience: 2 March 2022

Presentation Guidelines

The time allocated to each presentation will be:

Key-note: 35 minutes talk and 5 minutes for discussion

Oral Session: 15 minutes talk and 5 minutes for discussion

Please create the ZOOM account from the below URL.

- Creating a free Zoom Account <https://zoom.us/signup>
- Zoom help center <https://support.zoom.us/hc/en-us>

1. Preparing the Items to attend the symposia with using ZOOM

① Device

Zoom supports Windows, Mac, Linux, Android (smartphones, tablets, etc.), and iOS (iPad, iPhone, etc.). A video conference requires high CPU performance. If the performance is low, the video and audio may be interrupted, and the system may slow down. You can participate using a web browser without installing the Zoom app.

② Network

It would be desirable to have a cable or high - speed Wi - Fi connection to ensure network stability, but a reliable 3G/4G mobile phone network could also be used.

③ Microphone and speaker

We recommend using a headset (an earphone - microphone unit) for presentation and discussions. A built - in microphone/speaker could be used for presentation and discussion, but the use of an external speaker - microphone unit is recommended so that unnecessary echoes can be prevented.

④ Camera

Please prepare a camera (PC built-in camera, external USB camera). It is recommended that you turn on the camera during the speaking (speaker, questioner, chairperson). However,

participants (other than the speaker, the chairperson, and those asking questions during a Q&A session) refrain from transmitting video and save the bandwidth.

2. Setting the ZOOM

① Test the ZOOM

It is recommended that you test the system beforehand in a strong and stable network environment. Make sure also that audio messages can be sent and received without any problem.

<https://zoom.us/test>

② Settings the names

Participants are requested to include their names, as well as information regarding their affiliation so that the chairperson will be able to easily identify the speaker as follows.

- Speaker: program number_ Given Family name_ University
e.g.) 1-1_Taro Suzuki_KUTE
- Session Chair: Chair_ Given Family name_ University
e.g.) Chair_Hanako Honda_ KUTE
- Audience: Given Family name_ University
e.g.) Ichiro Toyota_ KUTE

3. Keynote and Oral Presentations Sessions

Please check your presentation timetables and enter the session. Follow the chairman's instructions to share the slides and start the presentation. Please be aware of the remaining time during the presentation, because the time will not be displayed on ZOOM.

Key-note: 35 minutes talk and 5 minutes for discussion

Oral Session: 15 minutes talk and 5 minutes for discussion.

- Saving, recording, and redistributing received video and presentation materials (including screen capture) are prohibited.
- If the audience has a question, use the raise hand icon feature of Zoom to tell the chairperson that you have a question. The chairperson will check the raised hand icon and nominate the questioner. When you are nominated, please turn on the microphone

and video, and ask the question.

→ During a meeting, navigate to the bottom options bar in your video screen and click Reactions. Underneath the reactions, there should be a separate button that says Raise Your Hand. Select this, and a hand icon should appear in the upper left-hand corner of your screen. To lower your hand, go back to Reactions, and the bottom button will now say Lower Your Hand. Select this to do so, and remove the hand icon from your video.

Committees

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Co-chairperson:

- Professor Li Lu: National University of Singapore, Singapore

Program committee

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Contact

Should you have any inquiries about this conference, please do not hesitate to contact us:

afmd@sc.kogakuin.ac.jp

Secretaries of symposia; Dr. Hsiang-Jung Wu and Dr. Hiroki Nagai

Program

Please log in to the following URL (ZOOM) for both days.

<https://zoom.us/j/93921967287?pwd=eTZWWUhYQmE0WVdvbWhQWVdjLzJzdz09>

Meeting ID: 939 2196 7287 Passcode: 889139

March 4 (Time: JST, KST; 0, CST, TST, SGT; -1, MSK; -6, GMT; -8)

Chair: Prof. Toshinori Okura (Kogakuin University of Technology and Engineering)		
13:00-13:10	Opening session	Opening Address: Prof. Mitsunobu Sato
13:10-13:50	Plenary 1	Prof. Li Lu (National University of Singapore) Challenges of Transition from Organic Liquid-based Rechargeable Batteries to Solid-state Rechargeable Batteries
13:50-14:10	Invite 1	Prof. Jiangfeng Ni (Soochow University) Advanced aqueous Cu-ion batteries for robust energy storage
14:10-14:30	Invite 2	Dr. Yumei Wang (National University of Singapore) Ferroelectric Engineered Electrode-Composite Polymer Electrolyte Interfaces for All-Solid-State Sodium Metal Battery
14:30-14:50	Invite 3	Prof. Jihuai Wu (Huaqiao University) Advanced Functional Materials in Dye-Sensitized Solar Cells
14:50-15:10	Break	
Chair: Prof. Tomohiro Yamaguchi (Kogakuin University of Technology and Engineering)		
15:10-15:30	Invite 4	Prof. Jin-Hyo Boo (Sungkyunkwan University) Ultra fast metal-free photocatalysts of partially oxidized 2D black phosphorus (2D-POVP) and MoS ₂ @BP 2D-nanocomposite
15:30-15:50	Invite 5	Prof. Hui Pan (University of Macau) Transition-metal compounds for Electrolysis of Water
15:50-16:10	Invite 6	Prof. Shu Yin (Tohoku University) Process Design for the Synthesis of Homogeneous Inorganic Nanomaterials
16:10-16:30	Invite 7	Prof. Yoshikazu Suzuki (University of Tsukuba) Development of Multilayer Ceramics as Ultrafiltration Membranes for Water-Soluble Polymer Separation
16:30-16:50	Invite 8	Dr. Ansgar Kretschmar (Forschungszentrum Jülich GmbH) Carbon nanofibers as a tailorable molecular sieve for CO ₂ separation
16:50-17:00	Break	
Chair: Prof. Mitsunobu Sato (Kogakuin University of Technology and Engineering)		
17:00-17:40	Plenary 2	Prof. Ruediger-A. Eichel (RWTH Aachen University) Advanced Solid Oxide Energy Conversion - from Materials Innovation to Versatile Devices

March 5 (Time: JST, KST; 0, CST, TST, SGT; -1, MSK; -6, GMT; -8)

Chair: Prof. Li Lu (National University of Singapore)				
13:00-13:40	Plenary 3	Prof. Mitsunobu Sato (Kogakuin University of Technology and Engineering) Research overview of the molecular precursor method		
	Room 1 (Chair: Dr. Yumei Wang)		Room 2 (Chair: Dr. Hsiang-Jung Wu)	
13:40-14:00	Oral 1	Mr. Kazuki Machida	Oral 7	Mr. Rodiawan
14:00-14:20	Oral 2	Mr. Yuhang Xin	Oral 8	Mr. Jun Endo
14:20-14:40	Oral 3	Mr. Yuji Yokomaku	Oral 9	Ms. Jingwen Wang
14:40-15:00	Oral 4	Mr. Meng Wang	Oral 10	Mr. Akito Taguchi
15:00-15:20	Oral 5	Mr. Hibiki Miyauchi	Oral 11	Mr. Nikolay I. Osipov
15:20-15:40	Oral 6	Mr. Yingshuai Wang		
15:40-16:00	Break			
Chair: Dr. Hideki Hashimoto (Kogakuin University of Technology and Engineering)				
16:00-16:20	Invite 10	Prof. Dongfeng Xue (Chinese Academy of Sciences) Preparation Theory and Technology of Large Size Crystal Materials		
16:20-16:40	Invite 11	Dr. Ryosuke S. S. Maki (Okayama University of Science) A further investigation of the complex M3 murataite structure using Hf substitution and STEM-EELS techniques		
16:40-17:00	Invite 12	Prof. Takeyoshi Onuma (Kogakuin University of Technology and Engineering) Fabrication of far-UV emitter around 200 nm using ultrawide bandgap semiconductors		
17:00-17:20	Invite 13	Dr. Chang-Lyoul Lee (Gwangju Institute of Science and Technology) Realizing Highly Stable Core-shell Perovskite Quantum Dots (QDs) and Light-Emitting Diode Applications		
17:20-17:40	Invite 14	Prof. Tomohiro Yamaguchi (Kogakuin University of Technology and Engineering) Impact of Ga _{1-x} In _x N underlayer for growth of Ga _{1-y} In _y N/Ga _{1-x} In _x N MQW structure		
17:40-18:00	Break			
Chair: Prof. Shu Yin (Tohoku University)				
18:00-18:20	Invite 9	Prof. Shibabrata Basak (Forschungszentrum Jülich GmbH) <i>In situ</i> TEM studies for making ideal batteries		
18:20-18:40	Invite 15	Prof. Serguei Savilov (Lomonosov Moscow State University) Local structure of carbon nanotubes consolidated by spark plasma sintering		
18:40-19:00	Invite 16	Dr. Alexander Ulyanov (Lomonosov Moscow State University) Temperature dependencies of paramagnetic response in carbon nanotubes. Local electronic structure		
Chair: Prof. Toshinori Okura (Kogakuin University of Technology and Engineering)				
19:00-19:10	Closing session	Closing Address: Prof. Mitsunobu Sato		

Challenges of Transition from Organic Liquid-based Rechargeable Batteries to Solid-state Rechargeable Batteries

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Abstract:

After thirty years of discovery of the commercial Li-ion rechargeable batteries, they have successfully been used in various applications, from small portable to large scale. The increased demand requires to explore and develop new energy storage devices from materials level as well as system level to meet high energy storage, high safety, and long operation in different conditions. One of many possible solutions is solid-state rechargeable battery where the flammable organic electrolyte is replaced by nonflammable or less flammable electrolyte. Although there are many achievements in recent years, there still exist a lot of challenges in order to really realize it in a commercial level. This presentation reviews and discusses the difficulties and challenges of solid-state rechargeable batteries.

Keywords: Solid-state battery; Solid electrolyte; Charge transfer

Research overview of the molecular precursor method

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Abstract:

In order to create a sustainable society, we need innovative technologies in which many research fields interact actively. High-performance thin films mounted on various devices such as computers, displays and so on, which have been developed mainly in the semiconductor industry, are quite useful for our daily life. Generally, those techniques require large equipment and high vacuum to produce high performance materials. If such highly functional thin films can be formed on large-area substrates by non-expensive chemical methods, it would be therefore enable to reduce raw materials and energy consumption.

In 1994, three years after I changed my base to Kogakuin University, my research group started industry-academia collaborative research on functional thin films. In that project, we contrived a new method for preparing excellent precursor solutions for metal-oxide thin films, by using only the stable and common metal complex salts. The method needs no preliminary process to form colloidal species via polymerization of metal ions, unlike as the sol-gel one. In 1996, we published our first research paper on Titania thin film formation in the "Molecular Precursor Method (MPM)" series.

To date, we have fortunately prepared the metal-oxide precursor solutions for more than 30 metal species and formed various functional thin films such as electron and ion conductors, semiconductors, and insulating materials, focusing mainly on metal oxides (Fig. 1). Biomaterials for hard tissue re-generation in aged society are also a part of our research since we achieved the apatite thin-film formation by the MPM. In this opportunity, I would like to introduce the research overview from the beginning of the MPM to the latest achievement.

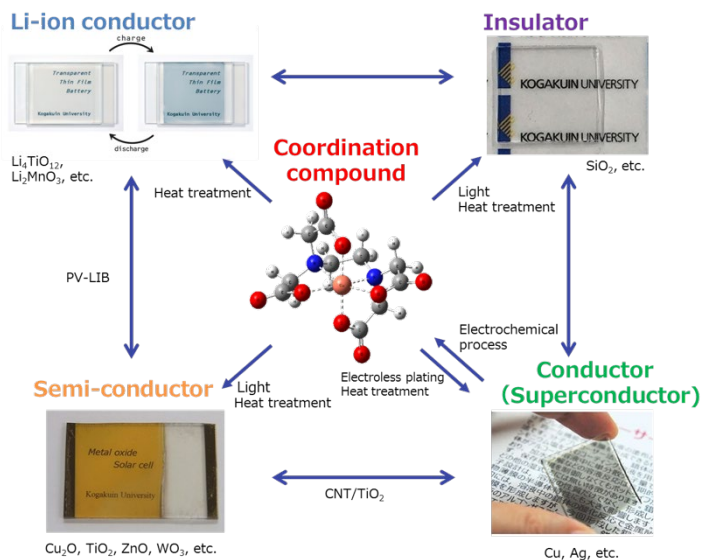


Fig. 1 Current research in Nano/Bio Materials Group.

The MPM is an interdisciplinary domain including applied physics and chemistry, materials science, and nanotechnology. It is important to note that the process of this method is both resource- and energy-saving one. I hope that this method might provide various thin films of high quality, supply useful devices, and contribute to achieve the sustainable society.

Keywords: Molecular Precursor Method, Thin film, metal complex, Sustainable society

Advanced aqueous Cu-ion batteries for robust energy storage

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Abstract:

The development of low-cost and high-energy aqueous battery technologies is of significance for renewable and stationary energy applications. However, this development has been bottlenecked by poor conductivity, low capacity, and limited cycling stability of existing electrode materials. Herein, we report on an energetic aqueous copper-ion system based on CuS, taking profit of high conductivity of CuS and efficient charge carrier of copper ions. Electrochemical results reveal a high capacity of 510 mAh g⁻¹, robust rate capability of 497 mAh g⁻¹ at a high rate of 7.5 A g⁻¹, and ultrastable cycling by retaining 91% of the initial capacity over 2500 cycles. The charge-storage mechanism of CuS was systematically investigated by ex-situ and in-situ techniques, involving a reversible transition from CuS to Cu₇S₄ and to Cu₂S through the redox of Cu²⁺/Cu⁺. Moreover, we demonstrate a hybrid ion battery consisting of a CuS cathode and Zn anode, which affords cell-level energy and power, respectively, of 286 Wh kg⁻¹ and 900 W kg⁻¹ exceeding many aqueous battery systems. Furthermore, we report that the topotactic anion exchange in CuS_{1-x}Se_x could considerably boost the electrochemical performance of CuS for robust Cu ion storage. Free-standing CuS_{0.5}Se_{0.5} nanosheets afford a high capacity of 491 mAh g⁻¹ and retain 80% of this capacity at an extremely high current rate of 20 A g⁻¹. The role of anion exchange in the electrochemical performance of CuS_{1-x}Se_x has been systematically investigated.

Keywords: Aqueous batteries; copper-ion battery; copper sulfide; copper sulfide selenide; electrochemical performance

Ferroelectric Engineered Electrode-Composite Polymer Electrolyte Interfaces for All-Solid-State Sodium Metal Battery

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Abstract:

With continuous improvements in ionic conductivity of the solid-state electrolytes, poor electrolyte-electrode compatibility and large interfacial impedances that limit the cyclic performances of batteries have become the main challenges for solid-state batteries. To enhance the compatibility between the polymer-based electrolytes and electrodes, and promote the interfacial ion conduction, we introduce a novel approach to engineer the interfaces between all-solid-state composite polymer electrolyte and electrodes using a thin layer of ferroelectrics. The well-designed and ferroelectric-engineered composite polymer electrolyte demonstrates an attractive ionic conductivity of $7.9 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. Furthermore, the ferroelectric engineering is able to effectively suppress the formation of solid electrolyte interphase at the interface between polymer electrolytes and Na metal electrode, and it can also enhance the ion diffusion across the electrolyte-ferroelectric-cathode/anode interfaces. Notably, an extraordinarily high discharge capacity of 160.3 mAh g^{-1} , with 97.4% in retention, is achieved in the ferroelectric-engineered all-solid-state Na metal cell after 165 cycles at room temperature. Moreover, outstanding stability is demonstrated that a high discharge capacity retention of 86.0% is achieved over 180 full charge/discharge cycles, even though the cell has been aged for 2 months. This work provides new insights in enhancing the long-cyclability and stability of solid-state rechargeable batteries.

Keywords: Solid-state batteries, Electrolyte-electrode interfaces, Ferroelectric engineering, Cyclic performance, Stability

Advanced Functional Materials in Dye-Sensitized Solar Cells

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Engineering Research Center of Environment-Friendly Functional Materials, Ministry of Education, Institute of Materials Physical Chemistry, Huaqiao University, Xiamen, 361021, China ¹Affiliation of

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Abstract: Dye sensitized titanium dioxide nanocrystalline solar cell (DSSC) is the research frontier of the third generation solar cell. With the support of the key projects of the National Natural Science Foundation of China and the National 863 program, the research group focus on the key technical issue such as efficiency, cost and stability, concentrate on the core science problems that photogenerated carriers is generated, migrated and collected in solar energy conversion, and carry out systematic research on the relationship among the composition and structure, the preparation and fabrication, the properties and performance of materials and device. Novel advanced functional materials including photoanode, electrolyte and anticathode are developed. Three significant scientific issues are clarified and ten important innovations are highlighted in this presentation.

In photoanode: The conversion luminescence and doping effect of rare earth ions in DSSC is demonstrated. The controllable growth of TiO₂ nanocrystalline mesoporous film and ultrathin layer is realized; Extracting organic dyes from natural plants as light absorbers for solar cells; The device performance is significantly improved by rare earth ion conversion luminescence and doping effect. In electrolyte: the interaction among matrix, solvent and ion in electrolyte, and the mutual restriction rule of fluidity, conductivity and stability are elucidated. Thermoplastic gel electrolytes based on polyvinyl alcohol and others are developed; Thermosetting gel electrolytes based on polyacrylic acid and others are developed; Poly(N-methyl-4-vinyl-pyridine iodine) solid polyelectrolyte is prepared; A UV responsive organic-inorganic hybrid heterojunction solar cell was developed. In anticathode: the relationship among electrode interface performance, catalytic activity, conductivity, light transmittance and photovoltaic performance are expounded. All titanium based rear illumination large area flexible solar cell is fabricated; Conductive polymer anticathodes such as polyaniline and polypyrrole are firstly prepared; A variety of novel Pt-free and Pt-less anticathodes with low cost, low impedance and good catalysis are developed.

Keywords: Dye-Sensitized Solar Cells; Advanced Functional Materials; Photoanode; Electrolytes; Anticathodes.

Ultra fast metal-free photocatalysts of partially oxidized 2D black phosphorus (2D-POVP) and MoS₂@BP 2D-nanocomposite

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Abstract:

Violet phosphorus (VP), also known as Hittorf's phosphorus, is promised a next-generation two-dimensional (2D) material with black phosphorus (BP). It is an intermediate in the process of synthesizing blacks starting with red phosphorus (RP), and has a unique activity. In this study, therefore, we synthesized the VP by a high energy mechanical milling method using RP powder. This synthesized VP, named as 2D-POVP, does not show up in both red and black, and has a catalytic reduction performance. The 2D-POVP had 2D amorphous structure with a very strong negative charge and the P=O structure acted as a redox functional group. The properties of the synthesized materials were confirmed by XRD, TEM, SEM, EDS, FT-IR, EPR, and Raman spectroscopy techniques. Dye materials were quantitatively analyzed by UV-Vis-spectrophotometer using methylene blue, rhodamine B, 4-nitrophenol, and their catalytic activities were measured using the synthesized 2D-POVP. This catalytic performance was further enhanced by the partially oxidized P=O structure and showed a recyclable performance by reducing the 30 mgL⁻¹ high concentration dye in a few minutes.

Since BP has proved problematic in the photocatalyst field, due to rapid recombination of electrons and holes. To overcome this, we used a nanocomposite with MoS₂ to prevent the recombination of electrons and holes and to have a broad range of optical absorption from visible light to near IR. MoS₂ nanoflakes are a two-dimensional (2D) material of the transition metal dichalcogenide family, the advantage of which is that it can be used as a nano-junction between 2D materials. The nanocomposite material of BP and MoS₂ shows a remarkable increase in photocatalytic decomposition ability of methylene blue which is an organic dye. It also has many cycles of catalytic ability, which is advantageous in terms of stability. There are expectations that MoS₂@BP photocatalysts will be widely applied as a nonprecious metal photocatalyst with broad light absorption spectra and multi-function photocatalytic materials. The objective of this study was to investigate the low cost and high efficiency metal-free reduction catalyst materials due to these advantageous characteristics.

Keywords: Metal-free photocatalyst, 2D phosphorus, MoS₂@BP nanocomposite, Catalytic ability.

Transition-metal compounds for Electrolysis of Water

Hui Pan

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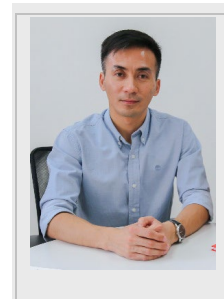
Abstract:

Electrocatalysis of water has been attracting increasing attention for hydrogen production because of its green, easily adoptable, and scale-up natures. However, the cost-to-energy efficiency is still limited for practical applications due to various factors. In this talk, we shall present the design and fabrication of novel electrocatalysts for oxygen and hydrogen evolution reaction with high catalytic performance. We found that: (1) the novel trimetallic nitride compound grown on nickel foam (CoVFeN@NF) showed an ultra-highly active OER activity, which was contributed by the formation of oxyhydroxide species on the surface of the catalyst due to surface reconstruction and phase transition; (2) three-dimensional porous hierarchical CoNiP/Co_xP multi-phase heterostructure on Ni foam exhibited ultra-highly catalytic activity for HER with an ultralow overpotential of 36 mV at 10 mA cm⁻², which was attributed to the strong electronic interaction at the heterointerface of CoNiP/CoP via the electron transfer from CoNiP to the heterointerface.; (3) the cobalt-iron nitride/alloy nanosheets grown on nickel foam (Co_xFe_yN/Co_xFe_y/NF) was a multisite catalyst for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER); (4) the active sites on the Ni/Ni_xP hybrids grown on carbon cloth (Ni/Ni_xP/CC) for HER in both acidic and alkaline conditions are negatively charged P ions. Our demonstrated that multimetal compound systems were catalytically active for OER and HER in electrochemical energy devices, which may find practical application in hydrogen-energy technologies.

Keywords: multimetal compounds; electrocatalysis of water; HER; OER; Surface reconstruction;

Biography

Dr. Hui Pan is a professor in the Institute of Applied Physics and Materials Engineering, and the founding head of Department of Physics and Chemistry in the Faculty of Science and Technology at the University of Macau. He got his PhD degree in Physics from the National University of Singapore in 2006. From 2006 to 2013, he worked at National University of Singapore as a Research Fellow, Oak Ridge National Laboratory (USA) as a Postdoctoral Fellow, and Institute of High Performance Computing (Singapore) as a Senior Scientist, respectively. He joined the University of Macau as an assistant professor in 2013. In his research, a combined computational and experimental method is used to design and fabricate novel nanomaterials for applications in energy conversion and storage (such as electro-/photo-catalysis, water splitting, N₂/CO₂ reduction, supercapacitors, hydrogen



The 9th Advanced Functional Materials & Devices (AFMD)

The 4th Symposium for Collaborative Research on Energy Science and Technology (SCREST) storage, solar cell, and fuel cells), electronic devices, spintronics, and quantum devices.

Acknowledgments

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Process Design for the Synthesis of Homogeneous Inorganic Nanomaterials

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IMRAM, Tohoku University, Japan

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Abstract:

It is accepted that inorganic nanomaterials usually are produced based on the dissolution-precipitation mechanism in the solution synthesis process. The water molecules have a significant influence on the crystal growth of nanomaterials, generally resulting in comparatively large particle size and hard agglomeration, because of its large dielectric constant. On the other hand, organic solvents usually produce smaller particles of the products because the low dielectric constants of organic solvents strongly relate to their lower solubility of the solute in the solution. Based on this principle, compared with the hydrothermal process, the solvothermal synthesis process has some advantages for the synthesis of nanosize materials. It has become a promising synthesis method for novel inorganic functional materials. The existence of water molecules during the solvothermal reaction significantly affects the uniformity of the reaction environment, so the amount of water and its homogeneous dispersion in the organic reaction solvent have a significant effect on the morphology, crystalline growth, and agglomeration status of the final product materials. In the present talk, a novel water molecular controlled release solvothermal process (WCRSP) for synthesizing homogeneous and morphology controllable inorganic materials will be introduced. Compared with the conventional synthesis method, it is found that the WCRSP process results in very homogeneous particles with unique morphologies and superstructures of the surface. The WCRSP process might be an effective method for the synthesis of various inorganic functional nanomaterials, such as TiO₂, CsWO₃, SnO₂, W₁₈O₄₉, etc. These particles possess controllable morphology and monodispersed particle size, resulting in some novel functionalities.

Keywords: Solvothermal synthesis; WCRSP, Oxides, Homogeneous, Morphology

Development of Multilayer Ceramics as Ultrafiltration Membranes for Water-Soluble Polymer Separation

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Abstract:

Porous ceramic membranes for separation and filtration utilize the excellent characteristics of ceramics such as thermal and chemical stability, high strength, corrosion resistance and so on. They are promising for the environmental protection, e.g. the water purification. To date, our group has focused on porous ceramic membranes prepared by MgAl₂O₄ spinel owing to its excellent thermal and chemical stability, and applied to microfiltration membranes (MF membranes, ~100 nm < d < ~10 μm) [1, 2]. More recently, we have successfully developed multilayer ceramics as ultrafiltration membranes (UF membranes, ~10 nm < d < ~100 nm) [3,4]. In this presentation, we demonstrate the removal/concentration of water-soluble polymer molecules by using these new multilayer MgAl₂O₄ ceramics. This work was supported by JSPS KAKENHI Grant Number JP16H04212 and 20H02431.

Keywords: MgAl₂O₄, filtration membrane, polyethylene oxide, porous ceramics, ultrafiltration

References

1. Y. Kamato and Y. Suzuki, "Reactively sintered porous MgAl₂O₄ for water-purification filter with controlled particle morphology," *Ceram. Int.*, **43**, 14090-14095 (2017). <https://doi.org/10.1016/j.ceramint.2017.07.145>
2. Y. Kamato, Y. Suzuki, "Reactive synthesis of porous MgAl₂O₄ membranes on a macroporous Al₂O₃-based ceramic tube toward cross-flow ultrafiltration," *J. Ceram. Soc. Jpn.*, **127** [4] 267-271 (2019). <http://doi.org/10.2109/jcersj2.18202>
3. Z. Ma and Y. Suzuki, "Hierarchical structure control of MgAl₂O₄ porous ceramics and application to organic polymer filtration membrane," *J. Am. Ceram. Soc.*, **104** [12] 6144-6154 (2021). <http://doi.org/10.1111/jace.18009>
4. K. Kagami, Y. Matsubayashi, T. Goto, J. Akedo and Y. Suzuki, "Nanoporous MgAl₂O₄ coating on porous Al₂O₃ support by aerosol deposition method for organic polymer filtration membrane," *J. Ceram. Soc. Jpn.*, accepted

Carbon nanofibers as a tailorable molecular sieve for CO₂ separation

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Abstract:

The climate change caused mainly by anthropogenic CO₂ emissions remains one of the most urgent challenges of our time. Despite avoiding CO₂ emitting technologies, the removal of CO₂ from flue gases, biogas or air with adsorption processes on suitable materials with high capacity and selectivity is a feasible option.

In our work, electrospun Polyacrylonitrile-based fibers were carbonized in Argon at various temperatures ranging from 600°C to 1100°C. On the resulting material various static gas adsorption experiments have been conducted, in order to elucidate the influence of the carbonization temperature on the gas adsorption properties, especially CO₂ adsorption capacity and selectivity. Whereas adsorption measurements with Argon yielded information about the pore size distribution, tests with CO₂ provided information on ultramicropores, adsorption energies, adsorption rate and the adsorption capacity. The adsorption selectivity of CO₂ over N₂ and CH₄, was evaluated with static and dynamic sorption methods. The surface chemistry was evaluated by XPS and elemental analysis, while structural changes were studied using diffraction methods in TEM.

Analyzing our data, a strong correlation of the CO₂ adsorption properties with the carbonization temperature was found and assigned to a change of the micropore size distribution and the surface functional groups. Especially for low carbonization temperatures the carbon nanofibers exhibit a very good low-pressure adsorption performance and excellent CO₂/N₂ selectivity.

For both Ar and CO₂ adsorption experiments, a sudden drop of adsorption capacity at a specific carbonization temperature was found. This effect was explained by a size exclusion effect in the ultramicropores of the carbon nanofibers, which depends on the size of the gas molecule and the carbonization temperature. Most recent measurements with additional ten adsorptives confirm that the carbon nanofibers can act as a molecular sieve, which can be steplessly tailored by means of the carbonization temperature during synthesis. This tailorable size exclusion effect allows to evaluate concepts for molecular sizes, which are often used to predict the accessibility of pores, for example the kinetic diameter. It could be concluded, that a frequently used set of values for the kinetic diameter comprises some drawbacks and alternatives from existing literature may be worth considering.

Keywords: Molecular Sieve, Carbon, CO₂ Adsorption, Electrospinning, Kinetic Diameter

***In situ* TEM studies for making ideal batteries**

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Abstract:

Safety features of Li-ion batteries are a high priority requirement as their adoption in electric vehicles and day-to-day electronic devices is continuously increasing. The liquid electrolytes that are typically used in traditional Li-ion batteries are flammable, especially at higher operating voltages and temperatures. By contrast, an all-solid-state battery (ASSB) makes use of solid electrolyte instead of liquid electrolyte, which reduces the risk of flammability. However, the solid-solid electrolyte-electrode interface in ASSBs introduces different sets of challenges from the traditional liquid-solid electrode-electrolyte interface. First, in batteries containing liquid electrolytes entire surface of electrode particles are wetted by electrolytes, whereas the electrode and solid electrolyte particles in ASSBs are connected primarily at point contacts, which are limited in terms of their numbers (as not all electrode particles are in direct contact with electrolyte particles), therefore ionic transport is basically restricted, diminishing the specific capacity of these batteries. Decomposition reactions at the electrode-electrolyte interfaces during battery cycling cause the formation of passivating layers and as well as electrode volume changes during battery cycling result in loss of contacts between electrode and electrolyte particles, further decreasing direct ion exchange pathways. Second, inhomogeneous (de)lithiation through point contacts can induce strain, which affects electrode mechanical integrity leading to capacity fade. *Operando* transmission electron microscopy (TEM) allows for the visualization of (de)lithiation processes in electrode materials at a single particle level in real-time. In our recent research, we have utilized the volume change property of Si nanoparticles during (de)lithiation to understand the interface kinetics of an ASSB during cycling. Following the safety aspect, aqueous based Zn-batteries are also gathering attention. In this respect, recent works on Zn-ion batteries using liquid phase TEM will also be discussed.

Keywords: *in situ* TEM, all-solid-state battery, liquid phase TEM, Zn-ion battery

Preparation Theory and Technology of Large Size Crystal Materials

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Abstract: Large size crystal materials such as single crystals, ceramic and glass materials are highly demanded in modern society. Preparation theory of large size crystal materials often involves multiscale problems, which strongly demand some cross-scale models to deal with multi-factor calculations. In this talk, I will summarize some recent progresses in the chemical bonding theory of single crystal growth and some pulling growth techniques of large size YAG, LYSO, LN crystals.

Keywords: chemical bonding theory of single crystal growth, large size crystal materials, preparation theory of large size crystal materials, preparation technology of large size crystal materials, lithium niobate, rare earth single crystals.

A further investigation of the complex M3 murataite structure using Hf substitution and STEM-EELS techniques

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Abstract:

Many members of the complex crystalline fluorite supercell structures (e.g. zirconolite, pyrochlore and murataite polytypes) have been considered for possible long-term radioactive-waste immobilization. The eight-coordinated sites in these crystals are of particular importance because they are preferred for the accommodation of trivalent rare earths and actinides present in radioactive waste from fuel element processing. The fluorite-type supercell structures include the murataites, M3, M5, M7 and M8, having those numbers of repeating fluorite sub-cell units. The reported formula of M3 is $^{[8]}Ca_1^{[8]}Ca_2^{[6]}Ti_1^{[5]}Ti_2^{[4]}AlO_{42}$, where $Ca = Ca, Mn, REE$; $Ti = Ti, Zr, Al$; $Al = Al, Fe$ with the originally assigned space group $F-43m$ (216) and $Z = 4$. We present here three methods of provisionally checking the complex M3 murataite structure and results that Zr is very likely not to be hosted in the $^{[6]}Ti$ site, but more likely replaces the $^{[8]}Ca_1$ site and less likely the $^{[8]}Ca_2$ site. One simple technique, as shown here, namely the substitution of Hf into the Zr site, is very helpful for structural analysis in these very complex cases in order to further illuminate the site preference of the Zr ion. This adjusted site preference for each cation from the powder X-ray diffraction (PXRD) agreed well with the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and element mapping results from the scanning transmission electron microscopy electron energy-loss spectroscopy (STEM-EELS) methods.

Keywords: M3-type murataite; Fluorite-type supercell structure; Powder X-ray diffraction (PXRD); High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM); Scanning transmission electron microscopy electron energy-loss spectroscopy (STEM-EELS).

Fabrication of far-UV emitter around 200 nm using ultrawide bandgap semiconductors

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Abstract:

Deep UV (DUV) and vacuum UV (VUV) light emitters have a variety of applications, such as in ozone cleaners, UV sterilization, etc. However, most of commercially available UV light sources in a wavelength range around 200 nm are discharge-type lamps or lasers. Therefore, development of ultrawide bandgap semiconductor-based far-UV light sources will be a technical breakthrough since their energy consumption is expected to be drastically reduced.

In this presentation, our strategy to develop the far-UV emitter and recent progress on growth of ultrawide bandgap materials and their far-UV emission characteristics will be briefly introduced. Here, the ultrawide bandgap materials include high-Al-content wurtzite-structured AlGaN alloys and high-Mg-content rocksalt-structured (RS) MgZnO alloys.

The AlGaN alloys are the most promising materials for deep-UV light emitters and their device performance is continuously developing. However, their characteristic optical anisotropy drastically reduces the light extraction efficiency from c-plane of Al-rich AlGaN alloys for the wavelength range shorter than 230 nm. Moreover, their shortest emission wavelength is limited to be around 210 nm for AlN. We use radio-frequency plasma-assisted molecular beam epitaxy (RF-MBE) as a growth technique. It is widely recognized that a control of group-III to nitrogen supply ratio is crucial for growth of high-AlN content AlGaN by RF-MBE, where special care has to be taken for the difference in the bonding energy of Ga-N and Al-N. Our recent progress will be briefly introduced in terms of its impact on the emission property.

The RS-MgZnO alloys are attracting attention as alternative candidate materials for DUV and VUV emitters by virtue of their wide variation of bandgap energy up to 7.7 eV for MgO. Recently, we demonstrated successful growths of atomically-flat single crystalline RS-MgZnO films on (100) MgO substrates by the mist chemical vapor deposition (mist CVD) method. Predominate observation of cathodoluminescence (CL) peak at around 199-210 nm was shown. Studies on their radiation pattern and power efficiency in the CL will be briefly introduced.

This work was supported in part by Grants-in-Aid for Scientific Research No. 20H00246 from MEXT, Japan.

Keywords: optoelectronics; ultrawide bandgap; semiconductor; growth; emission; deep UV.

Realizing Highly Stable Core-shell Perovskite Quantum Dots (QDs) and Light-Emitting Diode Applications

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Abstract:

Recently, perovskite quantum dots (QDs) have attracted intensive interest due to their outstanding optical properties, but their extremely poor chemical stabilities hinders the development of the high-performance perovskite QD-based light-emitting diodes (PeLEDs). In this study, chemically stable SiO₂ coated core-shell perovskite QDs are prepared to fabricate all-solution-processed PeLEDs. When the SiO₂ shell thickness increases, the chemical stability of perovskite QDs is dramatically improved, while the charge injection efficiency is significantly decreased, which becomes the biggest obstacle for PeLED applications. Thus, controlling the SiO₂ thickness is essential to obtain core-shell perovskite QDs optimal for PeLEDs in an aspect of chemical and optoelectrical properties. Optimization of the APTES/OAm ratio affords defect site (A site) doped CsPbBr₃ QDs with an ultrathin SiO₂ shell (A-CsPbBr₃@SiO₂ QDs) that exhibit longer radiative lifetimes and smaller shallow trap fraction than those without defect site (A site) doping, resulting in a higher photoluminescence quantum yield. The all-solution-processed PeLED is successfully fabricated under ambient conditions, facilitating perovskite QD utilization in low-cost, large-area, flexible next-generation displays.

Keywords: Perovskite quantum dots (QDs), Light-emitting diodes (LEDs), Core-shell structure, Ligand binding energy, Chemical stabilities

Impact of Ga_{1-x}In_xN underlayer for growth of Ga_{1-y}In_yN/Ga_{1-x}In_xN MQW structure

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Abstract:

GaInN alloys have been attracting considerable attention for application to not only blue and green but also red light-emitting devices such as light-emitting diodes (LEDs) and laser diodes (LDs). GaInN/GaN multi quantum well (MQW) structure, grown on top of GaN underlayer (UL), is used as an active region of blue and green light emitting devices. However, it is difficult to use this GaInN/GaN MQW structure in a red light-emitting device. One of the serious issues is considerable plastic relaxation due to large lattice mismatch between high In-content GaInN and GaN in the MQW structure. We have grown Ga_{1-y}In_yN/Ga_{1-x}In_xN (y>x) MQW structure on GaN UL. Since there still exists a large lattice mismatch between MQWs and GaN, Ga_{1-x}In_xN UL has been inserted between MQWs and GaN to suppress the plastic relaxation in the MQWs. In this study, the impact of Ga_{1-x}In_xN UL for the growth of Ga_{1-y}In_yN/Ga_{1-x}In_xN MQW structure is discussed.

Ga_{1-y}In_yN/Ga_{1-x}In_xN MQW structure was grown by radio-frequency plasma-assisted molecular beam epitaxy (RF-MBE) on a commercialized halide vapor phase epitaxy (HVPE)-grown (0001)GaN/α-Al₂O₃ template. A low-temperature Ga_{1-x}In_xN buffer layer with a thickness of approximately 10 nm was first grown at the substrate thermocouple temperature of 630°C. The effect of low-temperature GaInN buffer layer for enhancing the relaxation ratio of subsequent Ga_{1-x}In_xN UL was confirmed by *in-situ* X-ray diffraction (XRD) monitoring. The Ga_{1-x}In_xN UL with a thickness of 1 μm was then grown at 865°C. Finally, Ga_{1-y}In_yN (3 nm)/Ga_{1-x}In_xN (5 nm) MQW structure was grown at 765°C. As a reference, the MQW structure was also grown directly on GaN UL.

Table I shows the relaxation ratio to GaN, relaxation ratio to UL and averaged In composition of MQW structures grown on GaInN UL and GaN UL. By inserting GaInN UL, the relaxation ratio of MQWs to GaN was increased and that of MQWs to UL was inversely decreased. The averaged In composition of MQWs was increased. Figure 1 shows room temperature photoluminescence (PL) spectra of both samples. By inserting GaInN UL, PL intensity increased twice and peak position shifted toward longer wavelength from 560 nm (green) to 660 nm (red). Details of this mechanism are discussed.

Keywords: GaInN, MQW, RF-MBE, red light-emitting device

This work was partly supported by JSPS KAKENHI Grant Numbers #19H00874, #19K05298 and #20K05348.

Table I Relaxation ratio to GaN, relaxation ratio to UL and averaged In composition of MQW structures grown on GaInN UL and GaN UL.

	Relaxation ratio to GaN (%)	Relaxation ratio to UL (%)	In composition (%)
On GaInN UL	57.2	11.4	31.2
On GaN UL	22.1	22.1	25.5

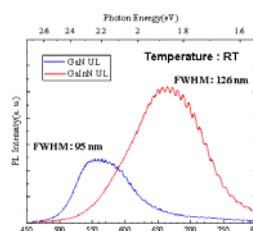


Fig.1 Room temperature PL spectra of samples with MQW structures grown on GaInN UL and GaN UL.

Local structure of carbon nanotubes consolidated by spark plasma sintering

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Abstract:

Spark plasma sintering (SPS) is a modern method for the consolidation of powders [1,2]. We report on the local electronic structure of the carbon nanotubes (CNT) consolidated by SPS and oxidized by boiling HNO₃ during 9.0 and 12.0 h. The structure was studied by the electron paramagnetic resonance (EPR), and characterized by transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

The appearance of holes and scraps (according to TEM data), and increase of the oxygen content from 17.7 to 20.4 at. % (according to XPS measurements) in consolidated CNTs with increasing the oxidation time from 9 to 12 h were observed. The change in intensity of Raman modes was detected with oxidation and attributed to the appearance of the defectiveness of the carbon tubes. The considerable changes in the EPR spectra with increase of oxidation time were observed. In brief, two components in the absorption EPR spectra lines were distinguished: narrow and broad components with different g-factors. It evidenced the different surrounding of paramagnetic centers attributed to the noted lines and associated with the localized and mobile electrons. The number of paramagnetic centers and linewidths, deduced from absorption spectra, increased with the oxidation.

Obtained results for the CNTs oxidized during 9.0 and 12.0 h will be analyzed and discussed considering the data for the not oxidized sample and compositions which were oxidized 3.0 and 6.0 h and studied in [2]. The analysis shows that if the oxidation time is longer than 6.0 h the structure of consolidated CNTs can be partially destroyed. It should be considered at designing the devices based on the consolidated CNTs.

Keywords: carbon nanotubes; spark plasma sintering; gas-phase oxidation; electron paramagnetic resonance; x-ray photoelectron spectroscopy; Raman spectroscopy

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1. M. Khoshghadam-Pireyousefan, A. Mohammadzadeh, A. Heidarzadeh, D. Brabazon, Fundamentals of Spark Plasma Sintering for Metallic, Ceramic, and Polymer Matrix Composites Production. Encyclopedia of Materials: Composites. 2021.
2. S. Saviolov, E. Suslova, V. Epishev, E. Tveritina, Y. Zhitnev, A. Ulyanov, K. Maslakov, O. Isaikina. Nanomaterials 11 (2021) 352.

Temperature dependencies of paramagnetic response in carbon nanotubes. Local electronic structure

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Abstract:

The properties of carbon nanomaterials (CNMs) depend on the variation of synthesis parameters: oxidation, substitution of carbon atoms by heteroatoms, the use of spark plasma sintering (SPS) for the sample consolidation. The increase in the oxidation time during the preparation of CNMs led to the increase in the amount of oxygen, the number of unpaired electrons and paramagnetic centers [1,2]. This in turn changes the properties of CNMs.

The electron paramagnetic resonance (EPR) is widely used method to study an interplay between the localized and mobile electrons in graphene oxides, nanoflakes and carbon fibers. At the same time, this technique was rarely applied to study carbon nanotubes (CNTs), and the various assignments of the absorption EPR lines to mobile and localized electrons were noted. We present here the EPR study of electronic local structure of oxidized CNTs consolidated with SPS to shed light on their conductivity, magnetism and spin density. CNTs were synthesized by pyrolytic decomposition of hexane.

The EPR measurements indicated that line intensity, g-factor and linewidth are temperature dependent values. The absorption spectra lines are split into broad and narrow components. The different g-factors of the lines display the different surrounding of paramagnetic centers attributed to them. The line intensity decreases with temperature while the linewidth increases and g-factor changes nonmonotonically. The inverse intensity of both lines is well described by Curie-Weiss law with some deviation indicating the superparamagnetic inclusions in the paramagnetic matrix. The attribution of the lines to localized or mobile electrons will be carefully discussed. The results will be compared with the results obtained for not-oxidized and oxidized samples.

The work was supported by the Russian Science Foundation (project No 21-43-00023).

Keywords: carbon nanotube, electron paramagnetic resonance, local electronic structure, mobile and localized electrons

1. S. Savilov et al., *Nanomaterials* **11**, 352 (2021).
2. A. Ulyanov, D. Stolbov, S. Savilov. *Z. Phys. Chem.* **236**, 79 (2022).

Design of Li-S battery for degradation control using LTO and SPAN electrode and investigation of the Li-doping technique by direct Li metal installation on electrodes

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Lithium-sulfur (Li-S) batteries as new secondary battery system have been attracted attention due to having high capacity of $1,672 \text{ mAhg}^{-1}$. Degradation of Li-S batteries is caused by dissolution of lithium polysulfide (Li_2S_m ; $2 < m < 8$) which is produced reaction intermediate of sulfur positive electrode during charge/discharge processes into electrolyte. The dissolution of Li_2S_m into electrolyte lead to significant degradation of cycle characteristics of Li-S batteries. In addition, the use of Li metal as negative electrode lead to the growth of Li dendrites during charge processes and contributes to short-circuit in Li-s batteries. In this study, for improve the performance of the Li-S battery, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as the negative electrode and sulfurized polyacrylonitrile (SPAN) as the positive electrode were applied to suppress Li-S battery degradation factors such as the groth of Li dendrite and dissolution of Li_2S_m . However, both LTO and SPAN electrode materials have no Li cation which can migrate between electrodes. Therefore, we applied direct installation of a suitable thin Li metal foil onto LTO or SPAN electrodes, such that the Li foil reduces the SPAN and LTO electrodes to enable doping of Li^+ into the positive / negative electrodes^[1].

The LTO negative electrode sheet was prepared by mixing, LTO, acetylene black(AB), and poly(vinylidene fluoride (PVDF) as following LTO : AB : PVDF = 85 : 7 : 8 (wt%). On the other hand, the SPAN positive electrode sheet was prepared by mixing SAPN, ketjen black (KB), carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR), as following SPAN : KB : CMC : SBR = 90 : 5 : 2.5 : 2.5 (wt%) For the cell preparation scheme (Fig. 1), the SPAN positive electrode, glass separator, 1M $\text{LiN}(\text{SO}_2\text{F})_2$ EC/DEC(=3/7) electrolyte, a LTO negative electrode and a capacity-regulated Li metal foil were encapsulated into coin-type cells (electrode capacity: LTO > Li metal > SPAN). The prepared cells were evaluated by galvanostatic charge/discharge at 303 K.

[LTO| Electrolyte | Li-on SPAN] cell (Fig.2) showed a negative potential at the Li doping process (black line), and exhibited stable charge/discharge profiles after the Li doping process. The obtained 1st discharge capacity was relatively low. The low discharge capacity suggests that Li wasn't completely doped in the Li-doping process. However, the increase of charge/discharge capacity suggests the use of remained Li metal. The proposed cell design method, which has active Li sources into electrode as reservoir, was exhibited possibility for applications.

Reference: [1] Y.Ushioda et al., *Chem. Lett.* **50**, 1217-1219 (2021).

Keywords: Lithium-Sulfur battery, Electrode material.

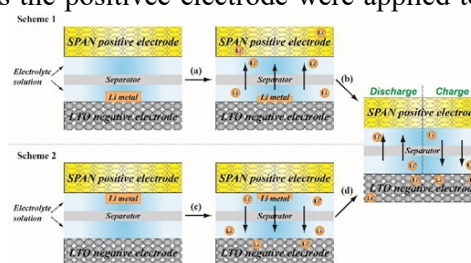


Fig. 1 Schematic images of installing Li metal on negative electrode or positive electrode.

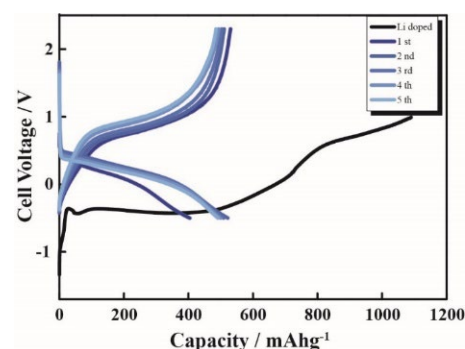


Fig. 2 Charge /discharge profiles of [LTO|Electrolyte|Li-on SPAN] cell.

High Voltage All-Solid-State Sodium Ion Battery

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Abstract Text

Currently there are two main ways to increase the capacity density of sodium ion batteries, 1) increase the voltage of the positive electrode and 2) increase the amount of sodium ions embedded in the negative electrode. The problem of more urgent need to solve is to enhance the voltage of the use of positive electrode, with a higher voltage of cobalt and nickel, has a lower elemental abundance, so how to enhance the voltage of high-abundance elemental materials is the focus of current research. The induced interaction between anions and transition metals is used to enhance the use voltage of iron-based materials to the order of 3.3 V (v.s. Na⁺/Na) for this type of electrode material. By taking advantage of the wide electrochemical window of solid electrolytes, changing the morphology of the material with the use of in situ solid state techniques, a nice tight contact at the atomic level can be obtained.

NASICON structural materials are a class of materials with fast ion sodium ion conducting pathways and are currently popular research materials as solid-state electrolytes for sodium ion batteries. While the conductivity of the material is sufficient, the problem of high interfacial resistance between the electrode and the solid-state electrolyte is the main reason that prevents NASICON structures from moving to practical production in all-solid-state sodium ion batteries. Surface modification of the material is an effective solution, but current surface modification methods do not satisfy the material contact at the atomic level and further introduce the problem of excessive polarization, so the use of in situ modification will facilitate the atomic level contact of the material and thus significantly reduce the impedance between the solid electrolyte and the electrode material.

The mixed pyrophosphate iron-based sodium ion battery cathode, because of its three-dimensional sodium ion diffusion channel and the effect of the polyanion group on iron effectively enhances the charge and discharge voltage platform of the iron-based material, but only 3 moles of sodium ions per mole of material can be released, which hinders the enhancement of the specific capacity of the material, so the introduction of other transition metal materials for enhancing the specific capacity of the material is a feasible way. An emerging hybrid pyrophosphate material is proposed, which is able to maintain 60% of the initial capacity after 2500 charge/discharge cycles and has good performance of high multiplicity.

Evaluation of Physicochemical and Electrochemical Properties of Gel Polymer Electrolyte for Sodium-Sulfur Batteries

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Introduction: The sodium-sulfur (Na-S) batteries have been commercialized as a high-capacity power storage system with a high abundance of resources, energy density, and long life. However, conventional Na-S batteries have to operate high temperature of about 573 K, which poses the problem of corrosion of the battery container and a severe fire risk.^[1,2] Therefore, low-temperature operating Na-S batteries are required. Gel polymer electrolyte (GPE), in which plasticizers are introduced into the solid polymer electrolyte, has been reported as one of the approaches for the low-temperature operation of Na-S batteries. However, GPE has the problem of weak mechanical strength and low thermal stability. In this study, we proposed GPE containing sulfolane, which has high thermal stability and oxidation resistance, and evaluated its physicochemical and electrochemical properties and Na-S battery performance.

Experimental: All samples were prepared in an Ar-filled glovebox. The GPEs were prepared using a P(EO/PO=8/2) as a matrix polymer, NaN(SO₂CF₃)₂ (NaTFSA) as an alkaline salt, DMPA as a photoinitiator, sulfolane (SL) as a solvent, respectively. The NaTFSA and SL were mixed at a molar ratio of NaTFSA : SL = 1 : x (x=2,3,4,5 and 6) and P(EO/PO) were mixed at a weight ratio of SL-based liquid electrolyte : P(EO/PO) = 7 : 3 to form a homogeneous solution. The solutions were spread on two glass plates separated by a Teflon sheet. The GPE thin films were fabricated by irradiation with UV light for 5 minutes to induce cross-linking of P(EO/PO). The ionic conductivities of GPEs were measured by an AC impedance analyzer. The Na-S batteries applying GPE were evaluated by a charge and discharge test at 333.15 K.

Result and Discussion: Fig.1 shows the temperature dependencies of ionic conductivity (σ) of the prepared GPEs at the cooling process. All GPEs exhibited higher σ values than that of P(EO/PO)-NaTFSA electrolytes at all temperatures. For example, σ values at 333.15 K were $8.8 \times 10^{-4} \text{ S cm}^{-1}$ (GPE, $x=2$) and $1.50 \times 10^{-4} \text{ S cm}^{-1}$ (P(EO/PO)-NaTFSA), respectively, and was confirmed the improvement effect for σ by SL electrolyte addition. Fig.2 shows the charge-discharge profiles of the prepared [Na | GPE ($x=2$) | SPAN] cell at 333.15 K and exhibited a reversible charge-discharge reaction and a high initial discharge capacity of ca. 360 mAh g^{-1} . Stable charge-discharge retentions were confirmed, even though slight noisy voltage operation was noted in the case of charge profiles. In this presentation, we will also report on electrochemical properties, such as the transference number of Na⁺ and time dependences of interfacial stabilization at the Na/GPE interface.

Reference

- [1] B. L. Ellis, L. F. Nazar, *Curr Opin Solid State Mater Sci.*, **16**, 168 (2012).
 [2] B. Dunn, H. Kamath, J.-M. Tarascon, *Science*, **334**, 928 (2011).

Keywords: Sodium-sulfur batteries, Gel polymer electrolyte, Electrochemistry

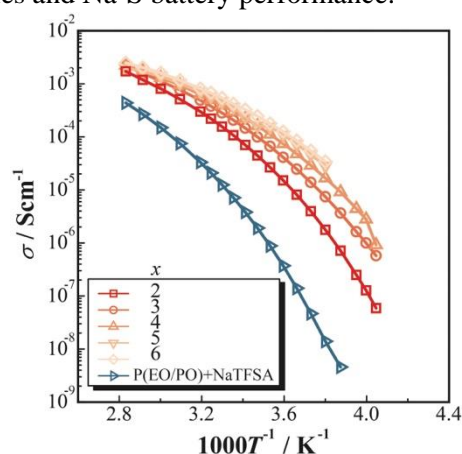


Fig.1 Temperature dependencies of ionic conductivity of GPEs for each composition.

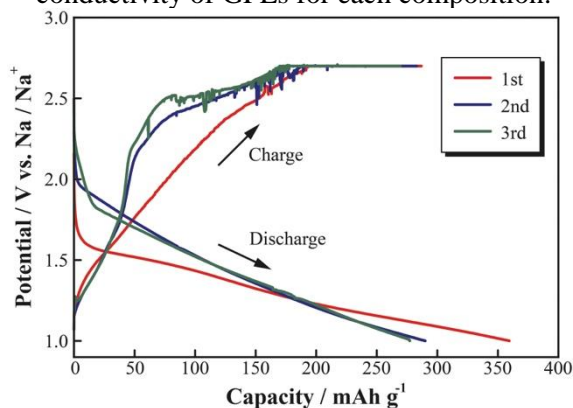


Fig.2 Charge-discharge profiles of [Na | GPE ($x=2$) | SPAN] cell at 333.15 K.

PVP-Assisted One-Step Hydrothermal Synthesis of Na₃V₂(PO₄)₂F₃/CNTs as Cathode Material for Na-Ion Batteries

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Abstract Text

Na-ion batteries (SIBs) have garnered tremendous interest due to their unique advantages of high safety, abundant Na resources, and low cost. Among the various cathodes, Na₃V₂(PO₄)₂F₃ (NVPF), a representative member of Na superionic conductor(NASICON) structured compounds, has been considered to be a promising candidate because of its superior structural stability, fast ion transport, high operating potential and so on. However, the poor-rate performance, resulting from its low conductivity, has become a massive obstacle to its practical application. In this work, carbon nanotubes(CNTs) together with morphology controlling were introduced to solve the issue of NVPF.

Generally, NVPF materials are mainly synthesized by solid-state high-temperature(480–850°C) reaction to obtain well-crystallized particles. Nevertheless, high temperature will result in that the NVPF particles become irregular, inhomogeneous or even agglomerate together to form larger clusters, which is unfavorable for the Na-ions transmission. Also, the F element may be lost during the calcination process, introducing some impurity phases such as Na₃V₂(PO₄)₃. Furthermore, the excess calcination process will greatly increase the energy consumption. Therefore, a green and cheap synthetic route for NVPF without additional calcination process should be developed urgently. Here, we propose a water based hydrothermal route to prepare well-crystallized NVPF, without any extra heat treatment process. Polyvinylpyrrolidone (PVP), known as a non-ionic surfactant, dissolved in water to reduce the polarity of the water, thus improving the dispersibility of NVPF particles and CNTs. In addition, the CNTs network improves electrolyte infiltration to decrease the internal diffusion resistance, and also provides fast transport pathways for electrons to enhance the poor electronic conductivity of the NVPF.

As-prepared well-crystallized NVPF/CNTs cathode material with tetragonal architecture exhibits excellent rate capability and cycling performance. The initial discharge specific capacity of the composite can reach 121.4 mAh g⁻¹ at 0.1 C. Even at a high current density of 5C, the capacity retentions are still over 85% even after 2000 cycles which corresponds to a very small capacity decay of 0.0075% per cycle. Significantly, the raw materials used in this method are very ordinary, cheap and eco-friendly. Therefore, we believe that this is a green, low cost, efficient, and facile method for the synthesis of NVPF cathode material.

Li⁺ Transport Properties of SL-based Gel Polymer Electrolyte and Effective Suppression of Lithium-polysulfide Dissolution in Li-S Batteries

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Abstract: Lithium-Sulfur (Li-S) batteries are attracting attention as high energy density secondary battery owing to high theoretical capacity (1,672 mAhg⁻¹) of elemental sulfur (S₈) as positive electrode active material. However, lithium polysulfides (Li₂S_n, n=2~8) of reaction intermediates dissolved into conventional organic liquid electrolyte and cause the redox shuttle effect. Sulfolane (SL) - based highly concentrated electrolyte was reported as Li₂S_n low soluble electrolyte^[1]. Therefore, we proposed quasi-solidification of SL-based highly concentrated electrolyte by using crosslinking polyether-based polymer, which was designed to suppress dissolution of Li₂S_n chemically and physically. In this study, the relationship between physicochemical properties and coordination structure were discussed for SL-based gel polymer electrolytes.

LiN(SO₂CF₃)₂ (LiTFSA) was dissolved into sulfolane (SL) as following molar ratio of x (=SL/LiTFSA) = 1, 1.5, and 2, respectively, and expressed x SL+1LiTFSA. x SL+1LiTFSA and P(EO/PO) macromonomer (EO/PO=8/2, M_w =ca.8000) were mixed as following x SL+1LiTFSA weight ratio of y = 70, 80, and 90 wt%, respectively, and 2,2 dimethoxy-2-phenylacetophenone was added as photoinitiator. Photopolymerization was carried out by UV irradiation for 5 min, self-standing and transparent gel polymer electrolytes (GPEs) were obtained. Thermogravimetry analysis and Raman spectroscopy were carried out for prepared GPEs.

Figure 1 shows the TG curves of prepared GPEs. Compared to neat SL, different weight decreasing tendencies were observed between 400 to 600K in TG curves of prepared GPEs. In all x values, thermal stability of GPEs were improved with y values. Thermal stability of liquid electrolytes should be improved in Li salt highly concentrated region owing to strong Li⁺ – solvent interaction. In the case of GPEs, interaction parts with Li⁺ cation should be located at both SL (=O) and host polymer (-O-). Therefore, no-coordinated SL molecules should be generated with the introduction of ether oxygen of P(EO/PO) and which should contribute decreasing thermal stability of GPEs. Figure 2 shows the Raman spectra of GPEs and liquid electrolyte in range of 540 - 610 cm⁻¹. Broad peaks around 565 – 590 cm⁻¹ were observed and attributed to δ SO₂ mode from SL. In previous works, the peaks shifts to high wavenumber in order of monodentate and bidentate SL structures with Li⁺, respectively^[1]. The peaks shifted to high wavenumber with y values in obtained Raman spectra, and therefore, increase of fraction of monodentate or non-coordinated SL molecules suggested by introduction of P(EO/PO).

[1] A. Nakanishi *et al.*, *J. Phys. Chem. C*, **123**, 14229-14238 (2019).

Keywords: Li-S Batteries, Gel Polymer Electrolyte

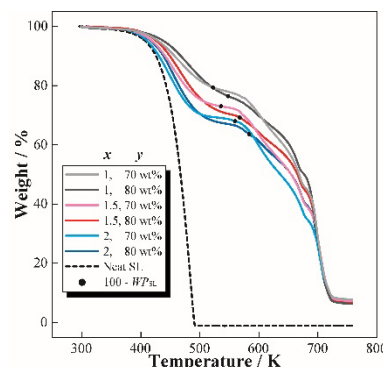


Figure 1 TG curves of prepared GPEs of $x=1\sim 2$, $y=70$ and 80 wt%.

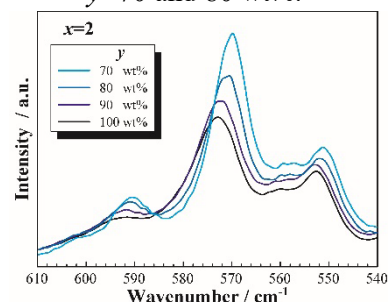


Figure 2 Raman spectra of $x=2$, $y=70$, 80 and 90 wt% and $x=2$ liquid electrolyte.

Effect of nitrogen doping on $\text{Na}_4\text{MnV}(\text{PO}_4)_3@C$ as high sodium storage properties cathode material for sodium-ion batteries

In order to reduce pollution during the use of fossil fuels, it is of great significance to develop sustainable renewable energy, as well as new power batteries and high-efficiency energy storage systems. Lithium-ion batteries (LIBs) have undoubtedly received the most attention, but their ever-increasing cost restricts the further development of LIBs. Sodium-ion batteries (SIBs) are expected to compete with LIBs.

At present, NASICON-type structured $\text{Na}_3\text{V}_2(\text{PO}_4)_3(\text{NVP})$ is a hot spot as a promising cathode material for sodium-ion batteries, which can provide a high reversible capacity and an energy density. However, due to the low conductivity of NVP, the capacity under high current density is low, and the relatively high cost of element V and its toxicity limit its application prospects. $\text{Na}_4\text{MnV}(\text{PO}_4)_3$ (NMVP) as its isostructural derivatives, exhibiting two flat voltage plateaus around 3.6 and 3.4 V and good capacity retention at high current densities, which indicates that NMVP is a very durable cathode for sodium ion batteries. However, this material also has poor electronic conductivity, which makes it difficult to achieve theoretical capacity. At present, the electronic conductivity can be improved by introducing carbon materials such as graphene or carbon nanotubes, but the high cost and cumbersome process of graphene or carbon nanotubes limit their further development.

Herein, the nitrogen-doped (N-doped) carbon coated NMVP ($\text{NMVP}@C-20N$) were prepared via a typical sol-gel approach. N-doped improves the electronic conductivity and sodium ion transport rate by introducing more defects and more active sites in the carbon layer, ultimately enhancing the sodium storage performance of the matrix material. Compared with $\text{NMVP}@C$, $\text{NMVP}@C-20N$ had good cycling and rate performance, especially at high current. At a current of 1 C (1 C = 110 mA g⁻¹), the initial capacities of $\text{NMVP}@C$, $\text{NMVP}@C-20N$ were 80 mAh g⁻¹ and 89 mAh g⁻¹ respectively. After 500 cycles, the capacity of $\text{NMVP}@C-20N$ still exhibited 85 mAh g⁻¹, which is much higher than the 61 mAh g⁻¹ of $\text{NMVP}@C$. At a high current of 10 C, the $\text{NMVP}@C-20N$ cathode still retained more than 82.9 % of the initial capacity after 2000 cycles.

Low Concentration of H₂S Gas Sensor Based on Au Nanoparticles Decorated SnO₂

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Abstract:

Hydrogen Sulfide (H₂S) is an undesirable gas because it can cause poisoning even at low concentrations. This study examined the performance improvement of the gas sensor at low concentration H₂S gas as the influence of 4 variations of Au nanoparticles concentration on SnO₂-based materials. To synthesize pure SnO₂ using simple thermal decomposition. The wet chemical method was used to dissolve the SnO₂ and Au before the dripping process to deposit viscous liquid on the electrodes in the following step. Characterization of materials was observed by XRD, SEM, and TEM. The results presented that a 40 ml of 50mM Au decoration was the best composition for an H₂S gas sensor with a sensing response of 65% at 0.2 ppm and 87% at 1.0 ppm (as shown in figure 1). The response time and the recovery time were 4 s and 31 s, respectively. In addition, the optimum working temperature of the sensing response was at 200°C (as presented in figure 2). The results of this experiment were possible for the sensor to be used in practical application

Keywords: gas sensor, SnO₂, Au decorated.

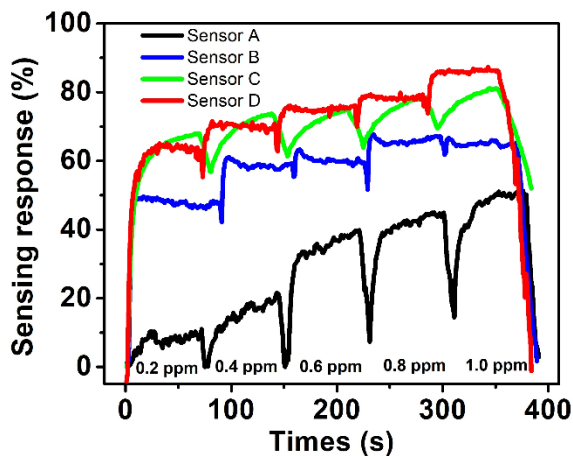


Figure 1. Sensing response of H₂S gas sensor with 4 variations concentration of Au nanoparticles.

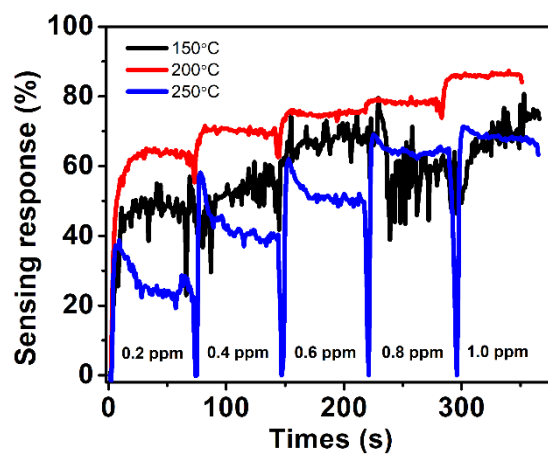


Figure 2. The optimum working temperature of the sensing response.

Reassessment of peak assignment of vibrational spectra for alkali phosphate crystals

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Abstract:

Phosphate glasses are used in a wide range of applications such as laser glass, optical lens, and sealing materials. Phosphate glasses are composed of PO₄ tetrahedral units, which are called Qⁿ units depending on the number of bridging oxygen atoms *n* (*n* = 0–3). Metaphosphate glasses are mainly composed of Q² units which form –P–O–P– chains and rings, but also contain Q¹ units. Glasses generally have isotropic structures, but some kinds of alkali metaphosphate glasses show significant anisotropy due to highly oriented –P–O–P– chains when the glass was deformed under uniaxial tensile stress above the glass transition temperature (*T_g*).¹ The significant anisotropy causes unique phenomena such as entropic shrinkage above *T_g* and improvement of mechanical properties.^{1,2} The relationships between structure and peak wavenumbers of vibrational spectra for phosphate crystals were used for peak assignment for phosphate glasses.^{3,4} In this study, Raman and IR spectra for alkali metaphosphate crystals with chains composed of Q² units and the alkali pyrophosphate crystal with dimers composed of Q¹ units were assessed by density functional theory (DFT) calculations.

Calculations of plane wave DFT of 50Li₂O–50P₂O₅, 50Na₂O–50P₂O₅, and 50K₂O–50P₂O₅ metaphosphate crystals, and 67Na₂O–33P₂O₅ pyrophosphate crystal (in mol%) were performed using the Quantum ESPRESSO (v6.6) package.⁵ The Perdew-Zunger exchange-correlation functional of the local density approximation was used. Pseudopotentials were norm-conserving scalar relativistic types.

The peak assignments of the calculated Raman and IR spectra were consistent with reported assignments except for the assignment of the peaks around 1100 cm⁻¹ of the calculated IR spectra for the alkali metaphosphate crystals.^{4,6–9} Peaks around 1100 cm⁻¹ of IR spectra have been assigned to asymmetric stretching vibrations of bonds between phosphorus atoms and non-bridging oxygens (NBO) of Q¹ units. However, the calculated IR spectra showed that the peaks around 1100 cm⁻¹ result from not only asymmetric stretching vibrations of P–NBO bonds of Q¹ units but also symmetric stretching vibrations of P–NBO bonds and asymmetric stretching vibrations of –P–O–P– bonds of Q² units.¹⁰

References

1. S. Inaba et al., *Nat. Mater.* **14** 312–317 (2015).
2. J. Endo et al., *J. Am. Ceram. Soc.* **98** 2767–2771 (2015).
3. E. I. Kamitsos et al., *Phys. Chem. Glasses*, **36** 141–149 (1995).
4. A. Rulmont et al., *Eur. J. Solid State Inorg. Chem.* **28** 207–219 (1991).
5. P. Giannozzi et al., *J. Phys.: Condens. Matter*, **21** 395502 (2009).
6. K. Griebenow et al., *J. Non-Cryst. Solids* **460** 136–145 (2017).
7. L. L. Velli et al., *Phys. Chem. Glasses* **46** 178–181 (2005).
8. K. Griebenow et al., *J. Non-Cryst. Solids* **481** 447–456 (2018).
9. G. L. Saouï et al., *J. Raman Spectrosc.* **33** 740–746 (2002).
10. J. Endo and Y. Suzuki, *J. Ceram. Soc. Jpn*, in press.

Keywords: Alkali metaphosphate crystal, Alkali pyrophosphate crystal, Raman spectrum, IR spectrum, Density functional theory (DFT), Quantum ESPRESSO.

Insights of morphology and facet exposure in perovskite CaSnO_3 as high-performance photocatalyst toward environmental remediation

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Abstract:

Exploring facile and novel methods to tailor the structure of materials on specific morphology has been attracted intensive interests. The structure-property relationship of a photocatalyst is highly related to the surface specific, in which the morphologies and crystal defect are crucial for the photocatalytic activity. It is necessary not only to enhance the performance of functional solid materials, but also to fundamentally study the relationship between surface electronic structure and the property. Perovskite oxides semiconductors were found to be alternative cost-effective green photocatalysts, which have attracted intense attention in the field of energy and environment because of their excellent tolerance, structural stability and controllable electronic state. CaSnO_3 with the perovskite structure is one of the alkaline-earth stannates, which has gained great interests due to its structural flexibility and thermal stability.

In this research, a mixture of NaCl and KCl was applied as a molten salt to fabricate CaSnO_3 with nanoparticle (CSO_NP), nanocube (CSO_NC) and cuboctahedron (CSO_CO) morphology. A small impurity of SnO_2 appeared in CaSnO_3 samples, which might be attributed to the surface enrichment of atomic tin. Anisotropic crystal growth rates lead to non-spherical structures, which are usually realized when the free surface energies of the various crystallographic planes are significantly different. The varied solutes led to the different dissolution rates of Ca^{2+} and Sn^{4+} ions, contributing to the diverse morphology of CaSnO_3 samples with different crystallographic orientation on the surface. In addition, the coordination property of CH_3COO^- from solute with Ca^{2+} or Sn^{2+} can change the free surface energy and further the growth rates of different crystal directions. CaSnO_3 samples with different morphology exhibited similar absorption edges around 320 nm, indicating only the UV light can be absorbed in this material. CaSnO_3 samples were tested for the photocatalytic degradation of methylene blue (MB). The MB solution turned from blue to transparent within 30 min over CSO_NP. In contrast, CSO_NC and CSO_CO decomposed MB dye by around 86% and 56% within 30 min, respectively. The higher specific surface area of CSO_NP compared with CSO_NC and CSO_OC is one of the reasons for the fast degradation rate. Also, the photoluminescence spectra showed that CSO_NP and CSO_NC exhibited low band edge emissions around 340-350 nm attributed to limited excitation recombination of charge carriers. The better photodegradation performance of CSO_NP and CSO_NC than CSO_CO indicated that the contribution of $\{100\}$ facets was greater than $\{111\}$ facets. The XPS and XANES results showed a decreased trend of $\text{Sn}^{2+}/\text{Sn}^{4+}$ ratios from CSO_NP to CSO_CO, which has an influence on the electronic structure and photocatalytic performance. The higher amount of Sn^{2+} in CSO_NP lattice led to the variation of lattice parameters and the distortion of SnO_6 octahedra, and subsequently improved the photocatalytic activity. This study shows that morphological control and defect mediation of semiconductors can induce preferential photocatalytic activity, which will open a new approach to design perovskite-type catalysts with high-performance.

Keywords: Stannate, perovskite, photocatalyst, morphology control, facet exposure

Spatially resolved cathodoluminescence studies on α - In_2O_3 films grown by mist CVD method

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Abstract:

In_2O_3 has two types of crystal structures: bixbite cubic In_2O_3 (c- In_2O_3) and rhombohedral corundum In_2O_3 (α - In_2O_3). Although α - In_2O_3 is a metastable phase, α - In_2O_3 can be applied in active elements of electronic devices because the bandgap energy that has been reported to be 3.7 eV [1] is much larger than that of c- In_2O_3 (≈ 3 eV) [2]. Single phase α - In_2O_3 films can be grown by mist chemical vapor deposition (mist CVD) method [3]. However, there have been few publications on the optical properties of single phase α - In_2O_3 films. In this presentation, the results of spatially resolved cathodoluminescence (SRCL) measurement on the α - In_2O_3 films grown by the mist CVD method will be shown.

Approximately 2.9- μm -thick single-phase α - In_2O_3 films were grown on (0001) α - Al_2O_3 substrates by mist CVD. The In_2O_3 powder was used as the source precursor, which was dissolved in deionized water using 37 % $\text{HCl}(\text{aq.})$. The solution was atomized using an ultrasonic transducer and the formed aerosol was transferred to the substrates using an oxygen carrier gas. The SRCL measurement was carried out using the system equipped on a scanning electron microscopy (SEM) under an acceleration voltage of -5 kV with the probe current of 500 pA at 100 K [4].

Figure 1(a) shows the surface SEM image for the single phase α - In_2O_3 film. A panchromatic SRCL image at 100 K is shown in Fig. 1(b). Figure 1(c) shows spot-excitation CL spectra at the positions numbered 1-5 in Fig. 1(a). The near-band-edge emission was not observed. Instead, a broad emission band was observed at around 2.3 eV, which nearly agreed with the previous report [5]. The local CL intensity appears to reflect the surface morphology, as revealed from Figs. 1(a) and 1(b). However, the peak energy was nearly unchanged in our single phase α - In_2O_3 film, as shown by the spot-excitation spectra in Fig. 1(c).

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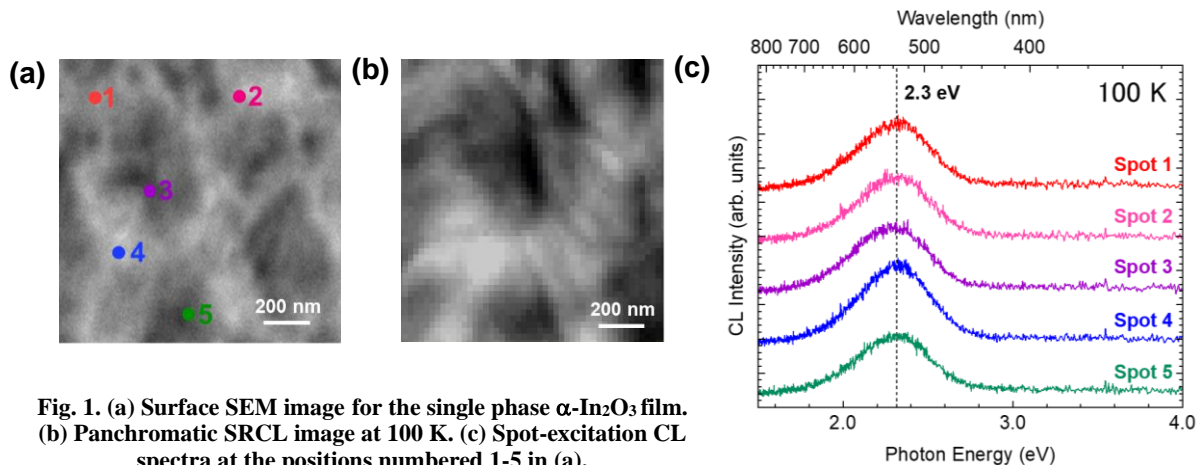


Fig. 1. (a) Surface SEM image for the single phase α - In_2O_3 film. (b) Panchromatic SRCL image at 100 K. (c) Spot-excitation CL spectra at the positions numbered 1-5 in (a).

Keywords: spatially resolved cathodoluminescence; α - In_2O_3 ; mist CVD

References: [1] N. Suzuki *et al.*, J. Cryst. Growth **401**, 670 (2014). [2] P. D. C. King *et al.*, Phys. Rev. B **79**, 205211 (2009). [3] N. Suzuki *et al.*, J. Cryst. Growth **364**, 30 (2013). [4] L. Y. Li *et al.*, Appl. Phys. Lett. **119**, 091105 (2021). [5] T. Nagata *et al.*, Jpn. J. Appl. Phys. **59**, SIIG12 (2020).

Hydrothermal synthesis of manganese (IV) oxides for supercapacitor application

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Abstract:

The rapid growth of the global economy has significantly enhanced the demands for energy consumption. Supercapacitors have been attracted interest due to great cyclability, fast charging/discharging rate, tremendous power density and compatibility with Green Chemistry principles. Charge accumulation in supercapacitors is realized through electrostatic adsorption of electrolyte ions in porous structure of the electrode (double-layer supercapacitors) or Faradaic redox reactions (pseudocapacitors). Transition metal oxides have been widely used as the electrode materials of pseudocapacitors. MnO₂-based materials are promising due to its high theoretical specific capacitance of 1370 F·g⁻¹, low cost and nontoxicity [1].

This work is devoted to hydrothermal synthesis of MnO₂. Temperature (100-160°C), reaction time (4-24 hours) and MnCl₂/KMnO₄ ratio were varied to optimize synthesis conditions of different MnO₂ modifications and control their morphology. Produced materials were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), low temperature nitrogen adsorption and cyclic voltammetry. According XRD results, α-MnO₂ and K_xMn_yO₂ with the structure of birnessite were obtained. It was found that increasing temperature of hydrothermal treatment leads to formation of α-MnO₂ and morphology changes from nanorods to nanoflakes (Figure 1). Synthesized oxides were tested as the electrode material for supercapacitors. Specific capacitance of obtained materials was achieved 120 F·g⁻¹ at 1 mV·s⁻¹ with potential window of 0.8 V (vs. Ag/AgCl) in 0.5 M Na₂SO₄ aqueous electrolyte.

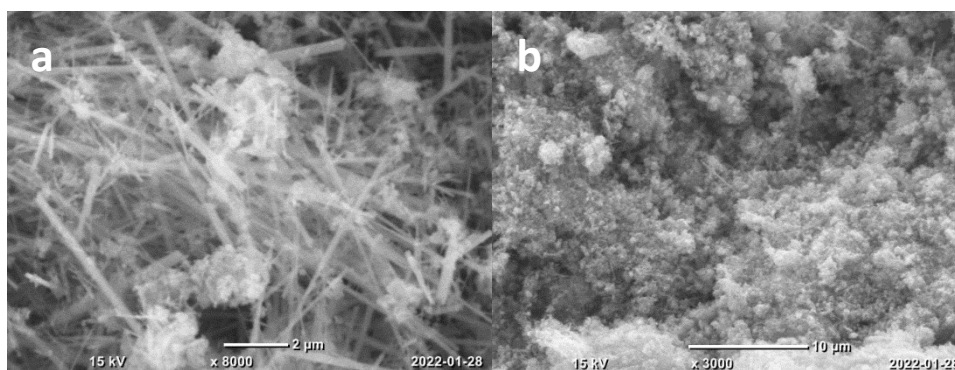


Figure 1. SEM micrographs of MnO₂ with different morphology: nanorods (a) and nanoflakes (b).

Keywords: supercapacitors, MnO₂.

References

[1] X. Bai, X. Tong, Y. Gao, W. Zhu, C. Fu, J. Ma, T. Tan, C. Wang, Y. Luo, H. Sun *Electrochim. Acta* **2018**, 281, 525-533

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