Kick-Off Meeting

of

EPSRC-JSPS Core-to-Core Collaboration in Advanced Materials

International Network on Polyoxometalate Science

for Advanced Energy Materials

and

NANOXCAT French-Japan International Associate Laboratory

Date: 17th and 18th July, 2019
International Conference Center Hiroshima, Hiroshima, Japan
(http://www.pcf.city.hiroshima.jp/icch/english.html)

17th July

8:30 – 11:30	Local Trip (Hiroshima Peace Memorial Park and Museum)	
11:30 – 12:30	**Lunch**	

Kick-Off Meeting of EPSRC-JSPS Core-to-Core Collaboration in Advanced Materials: International Network on Polyoxometalate Science for Advanced Energy Materials

12:30 – 12:45	**Opening Remarks**	
12:45 – 13:05	John Errington	Newcastle University
13:05 – 13:25	Elizabeth Gibson	Newcastle University
13:25 – 13:45	Graham Newton	University of Nottingham
13:45 – 14:05	Darren Walsh	University of Nottingham
14:05 – 14:25	Laia Vila-Nadal	University of Glasgow
14:25 – 14:35	**Coffee Break**	
14:35 – 14:55	Haralampos N. Miras	University of Glasgow
14:55 – 15:15	Lee Johnson	University of Nottingham
15:15 – 15:35	Hong-Ying Zang	Northeast Normal University
15:35 – 15:55	Li-Kai Yan	Northeast Normal University
15:55 – 16:15	Tomoji Ozeki	Nihon University
16:15 – 16:25	**Coffee Break**	

16:25 – 16:40	Kenji Ohashi	Nihon University
16:40 – 16:55	Osamu Tomita	Kyoto University
16:55 – 17:10	Satoshi Ishikawa	Kanagawa University
17:10 – 17:25	Yuji Kikukawa	Kanazawa University
17:25 – 17:40	Kosuke Suzuki	The University of Tokyo
17:40 – 17:55	Masahiro Sadakane	Hiroshima University

19:00 – **Reception**

Hiroshima ORIZURU Tower

https://www.orizurutower.jp/en/

18th July

8:30 – 8:50	Manuel Lechner	Ulm University
8:50 – 9:10	Sébastien Paul	Ecole Centrale de Lille
9:10 – 9:30	Guillaume Izzet	Sorbonne University
9:30 – 9:45	Wataru Ueda	Kanagawa University
9:45 – 10:00	Hiroki Miyaoka	Hiroshima University
10:00 – 10:15	Ryu Abe	Kyoto University
10:15 – 10:25	**Coffee Break**	
10:25 – 10:40	Wataru Ninomiya	Mitsubishi Chemical Corporation
10:40 – 10:55	Takeru Ito	Tokai University
10:55 – 11:10	Hirofumi Yoshikawa	Kwansei Gakuin University
11:10 – 11:25	Atsushi Yagasaki	Kwansei Gakuin University
11:25 – 11:40	Tadaharu Ueda	Kochi University
11:40 – 11:55	Yoshihito Hayashi	Kanazawa University
11:55 – 12:10	Sayaka Uchida	The University of Tokyo
12:10 – 12:25	**Closing Remarks**	
12:25 – 13:20	**Lunch**	
13:20 – 14:00	**Core-to-Core Management committee Meeting**	

Kick-Off Meeting of NANOXCAT French-Japan International Associate Laboratory

15:00 – 15:15	Sébastien Paul	Ecole Centrale de Lille
	General aspect of LIA NANOXCAT	
15:15 – 15: 30	Franck Dumeignil	Université de Lille
	Hybrid Catalysis as a New Concept for Upgrading Biomass-Derived Molecules	
15:30 – 15:45	Mickael Capron	Université de Lille
	What’s the right catalyst choice and the ad-hoc reaction conditions for a target molecule from glycerol oxidation?	
15:45 – 16:00	Masahiro Sadakane	Hiroshima University
	Results in the last year: Synthesis of PMoBi oxide	
16:00 – 16:30	Discussions	

Welcome to Hiroshima.

Thank you very much for coming to our joint kick-off meeting of EPSRC-JSPS Core-to-Core Collaboration in Advanced Materials: International Network on Polyoxometalate Science for Advanced Energy Materials and NANOXCAT French-Japan International Associate Laboratory. The Core-to-Core Program is designed to create world-class research hubs in research fields considered to be cutting-edge and internationally important. This program supports join research, seminars, and scientist exchange between us for 5 years. I hope we can have fruitful collaborations.

Current partners are

Japan: Hiroshima University (Coordinator: Masahiro Sadakane), Nihon University, Kyoto University, Kanagawa University, Kanazawa University, The University of Tokyo, Mitsubishi Chemical Corporation, Tokai University, Kwansei Gakuin University, Kochi University, Chubu University, Kyushu University, Tokyo Institute of Technology, Wakayama University, Yamaguchi University, The National Institute of Advanced Industrial Science and Technology (AIST), Japan Synchrotron Radiation Institute (JASRI), and Nippon Inorganic Colour & Chemical Co., Ltd

UK: Newcastle University (Coordinator: John Errington), University of Nottingham, University of Glasgow

France: Ecole Centrale de Lille (Coordinator: Sébastien Paul) and Sorbonne University

Germany: Ulm University (Coordinator: Carsten Streb) and Friedrich-Schiller University Jena

China: Northeast Normal University (Coordinator: Yang-Guang Li)

Masahiro Sadakane
Department of Applied Chemistry,
Graduate School of Engineering
Hiroshima University

研究拠点形成事業
Core-to-Core Program

EPSRC
Engineering and Physical Sciences
Research Council

CNRS

CATALIGHT

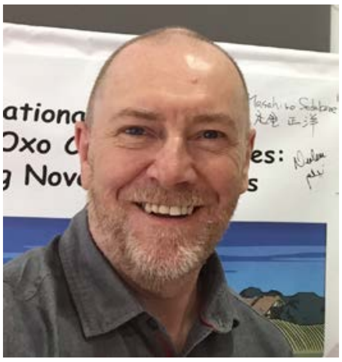
NSFC
National Natural Science
Foundation of China

UK

Newcastle University

University of Nottingham

University of Glasgow

<table>
<tr><td rowspan="4"> </td><td>R. John Errington</td></tr>
<tr><td>Reader in Metalorganic Chemistry
Newcastle University</td></tr>
<tr><td>John.Errington@ncl.ac.uk</td></tr>
<tr><td>www.ncl.ac.uk/nes/staff/profile/johnerrington.html</td></tr>
</table>

Research keywords: Polyoxometalates; synthesis; hybrids; reactivity; non-aqueous; proton-transfer; electron-rich; catalysis; ^{17}O NMR.

The advancement of polyoxometalate (POM) science requires rational routes to targeted structures and compositions for systematic studies of reactivity and properties, and our new synthetic methodologies and associated ^{17}O-enrichment techniques are enabling detailed solution studies of reactive POMs. [1, 2] The resulting access to homologous series of POMs is revealing the consequences of atom substitution within structural frameworks and provides the basis for theoretical DFT studies and a deeper understanding of subtle electronic effects and bonding variations. [3] A detailed understanding of proton and electron transfer processes is emerging from studies of protolytic reactions in POM-catalysed reactions, *e.g.* alkene epoxidation with H_2O_2, [4] and investigations of non-aqueous reduction are providing electron-rich and super-reduced POMs. [5] We are also exploring the self-assembly and templating properties of amphiphilic POMs, multifunctional catalysts that exploit the synergy created by incorporation of POMs at interfaces, and the design and synthesis of highly active POMs for small molecule activation. [6]

References.

[1] R. J. Errington, *Adv. Inorg. Chem.* 2017, **69**, 287-336.

[2] R. J. Errington, B. Kandasamy, D. Lebbie and T. Izuagie, *Structure and Bonding*, 2018, **176**, 139-163.

[3] B. Kandasamy, P. G. Bruce, W. Clegg, R. W. Harrington, A. Rodríguez-Fortea, M. Pascual-Borrás and R. J. Errington, *Chem. Eur. J.* 2018, **24**, 2750-2757.

[4] N. V. Maksimchuk, I. D. Ivanchikova, G. M. Maksimov, I. V. Eltsov, V. Yu. Evtushok, O. A. Kholdeeva, D. Lebbie, R. J. Errington, A. Solé-Daura, J. M. Poblet, and J. J. Carbó, *ACS Catalysis*, 2019, **9**, 6262-6275

[4] R. Canioni, E. Cadot, R. J. Errington, N. Leclerc-Laronze and C. Roch-Marchal, *Curr. Inorg. Chem.* 2017, **7**, 13-20.

[6] P. Klonowski, J. C. Goloboy, F. Uribe-Romo, F. Sun, L. Zhu, F. Gándara, C. Wills, R. J. Errington, O. M. Yaghi, and W. G. Klemperer. *Inorg. Chem.* 2014, **53**, 13239-13246.

	Elizabeth A. Gibson (Libby)
	Reader in Energy Materials
	elizabeth.gibson@ncl.ac.uk
	https://research.ncl.ac.uk/p-type/

Research keywords: Artificial Photosynthesis, Tandem dye-sensitized solar cells, Supramolecular Photochemistry, Photocatalysis, Transient spectroscopy, Spectroelectrochemistry.

Efficient dye-sensitized photocathodes offer new opportunities for converting sunlight into storable energy cheaply and sustainably.[1] We are developing dye-sensitized NiO cathodes for the photo-reduction of carbon dioxide or water to high energy products (solar fuels) using the lessons we have learnt from solar cells.[2] The potential advantage of this strategy is it exploits the selectivity of a molecular catalyst in a robust device. Assembling two photoelectrodes in a tandem configuration (see figure) enables water oxidation at the photoanode to supply electrons to the photocathode to be consumed in the reduction of e.g. H^+ to H_2. Generating hydrogen on one electrode and oxygen on another enables the two gasses to be collected separately. Additionally, by separating the functions of light absorption, charge transport and catalysis between the colloidal semiconductor and molecular components, the activity of each can be optimised, rather than relying on one material to have all the necessary credentials. We are tackling the main limitations to photocurrent, by improving the quality of the NiO electrodes [3] and engineering new photocatalysts, to increase the quantum efficiency of the device. The electron-transfer dynamics are key to the performance and a major challenge is slowing down charge recombination between the photoreduced dye and the oxidised NiO so that chemistry can take place.[4] Highlights from recent work include examining charge-transfer at the interface between NiO and new supramolecular photocatalysts using transient absorption spectroscopy and time-resolved infrared spectroscopy.

References

[1] E. A. Gibson, *Chem. Soc. Rev.*, **2017**, 46, 6194 – 6209,

[2] N. Põldme, L. O'Reilly, I. Fletcher, I. Sazanovich, M. Towrie, C. Long, J. G. Vos, M. T. Pryce, E. A. Gibson *Chem. Sci.*, **2019**,10, 99-112.

[3] C. J. Wood, G. H. Summers, C. A. Clark, N. Kaeffer, M. Braeutigam, L. R. Carbone, L. D’Amario, K. Fan, Y. Farré, S. Narbey, F. Oswald, L. A. Stevens, C. D. J. Parmenter, M. W. Fay, A. La Torre, C. E. Snape, B. Dietzek, D. Dini, L. Hammarström, Y. Pellegrin, F. Odobel, L. Sun, V. Artero, E. A. Gibson, *PCCP*, **2016**, 18, 10727 – 10738. Dini, D.; Halpin, Y.; Vos, J. G.; Gibson, E. A.; *Coord. Chem. Rev*., 2015, 304-305, 179-201.

[4] F. A. Black, A. Jacquart, G. Toupalas, S. Alves, A. Proust, I. P. Clark, E. A. Gibson, G. Izzet *Chem. Sci.* **2018**, 9, 5578-5584.

Tom Penfold

Lecturer in Computational and Theoretical Chemistry, Newcastle University

tom.penfold@ncl.ac.uk

http://penfoldgroup.co.uk

Research keywords: Excited State Dynamics, Quantum Dynamics, Molecular Dynamics, Energy and Electron transfer, X-ray Spectroscopy.

Research in my group focused upon computational and theoretical chemistry to deliver detailed understanding of non-equilibrium molecular and materials properties. The research interests of the group are focused upon developing methods for and understanding excited state properties, nonadiabatic ultrafast dynamics and time-resolved spectroscopy. We have strong expertise in X-ray spectroscopy and molecular dynamics. Through the North East Centre of Energy Materials (NECEM) project, we are studying charge transfer across interfaces. This includes detailed studies into the coupled nuclear and electronic dynamics associated with electron transfer into polyoxometalates.

References

[1] T. J. Penfold, E. Gindensperger, C. Daniel and C. M. Marian, Spin-Vibronic Mechanism for Intersystem Crossing., Chem. Rev., **118**:6975 (2018).

[2] T. J. Penfold, F. Diaz and A. Monkman, The Theory of Thermally Activated Delayed Fluorescence for Organic Light Emitting Diodes., Chem. Commun., **54:** 3926 - 3935 (2018).

[3] T.J. Penfold, J. Szlachetko, F. G. Santomauro, A. Britz, W. Gawelda, G. Doumy, A.M. March, S.H. Southworth, J. Rittmann, R. Abela, M. Chergui and C.J. Milne. Revealing hole trapping in zinc oxide nanoparticles by time-resolved X-ray spectroscopy. Nat. Commun. **9:**478 (2018).

[4] G. Capano, C.J. Milne M. Chergui, U. Rothlisberger, I.Tavernelli and T.J. Penfold* Probing Wavepacket Dynamics using Ultrafast X-ray Spectroscopy. J. Phys. B 48:214001 (2015).

	Dr Michael Richard Probert
	Senior Lecturer in Inorganic Chemistry and Head of Crystallography, Newcastle University
	michael.probert@ncl.ac.uk
	https://www.staff.ncl.ac.uk/michaelprobert/

Research keywords: diffraction, extreme conditions, solid state, crystallization, polymorphism, instrumentation development, molecular and extended structures

Mike’s research interests include: studying the structure/property correlations of molecular systems under extreme conditions, ranging from simple organic compounds that exist as liquids under ambient conditions, to complex multi-dimensional systems that undergo novel phase changes upon cooling and/or the application of pressure; the polymorphic nature of compounds in the solid state; and the accurate experimental determination of electron densities of crystalline materials. These areas are all aided by the development of highly specialised equipment and novel experimental design that form another aspect to his research portfolio.

Web of Science ResearcherID: http://www.researcherid.com/rid/G-5899-2014
Publons: https://publons.com/researcher/2522774/michael-r-probert/
ORCID iD: https://orcid.org/0000-0002-2412-7917

	Graham Newton
	Assistant Professor of Inorganic and Materials Chemistry, University of Nottingham
	graham.newton@nottingham.ac.uk
	Newtonchemistry.com

Research keywords: Organic-inorganic hybrid metal oxide clusters, coordination chemistry, molecular switches, photocatalysis, supramolecular chemistry, redox materials, energy storage

My group is interested in the manipulation of the electronic structure, redox properties, photochemistry, and self-assembly behavior of molecular metal oxides and their analogues.[1-3] This can be achieved in a number of ways, but our key approach is through the preparation of organic-inorganic hybrid molecular metal oxides, the physical properties of which depend on the interplay of their organic and inorganic building blocks. We are then particularly interested in studying how those molecular properties can be transferred across the size scales, from molecular to nanoscale and through to macroscale functional materials.[4]

I would be particularly interested in exploring potential collaborations in the areas of catalysis and photocatalysis, and functional nanomaterials.

References

1. K. Kastner, A. J. Kibler, E. Karjalainen, J. A. Fernandes, V. Sans and G. N. Newton (**2017**). "Redox-active organic–inorganic hybrid polyoxometalate micelles." *J. Mater. Chem. A* 5(23): 11577-11581
2. J. M. Cameron, S. Fujimoto, K. Kastner, R.-J. Wei, D. Robinson, V. Sans, G. N. Newton and H. Oshio (**2017**). "Orbital Engineering: Photoactivation of an Organofunctionalized Polyoxotungstate." *Chem. Eur. J.* 23(1): 47-50
3. G. N. Newton, S. Yamashita, K. Hasumi, J. Matsuno, N. Yoshida, M. Nihei, T. Shiga, M. Nakano, H. Nojiri, W. Wernsdorfer and H. Oshio (**2011**). "Redox-Controlled Magnetic $\{Mn_{13}\}$ Keggin Systems." *Angew. Chem. Int. Ed.* 50(25): 5715-5719
4. D. J. Wales, Q. Cao, K. Kastner, E. Karjalainen, G. N. Newton and V. Sans (**2018**). "3D-Printable Photochromic Molecular Materials for Reversible Information Storage." *Adv. Mater.* 30(26)

	Darren Walsh
	Associate Professor of Physical Chemistry, University of Nottingham
	darren.walsh@nottingham.ac.uk
	electrochemistry.co.uk

Research keywords: electrochemistry, ionic liquid, electrocatalysis, redox materials, energy storage

My group is interested in the application of electrochemical methods to chemical problems. We are especially interested in the development of new materials for electrochemical energy storage and conversion. We develop new electrolytes, electrode materials, and redox mediators for batteries, fuel cells, electrolyzers and supercapacitors. We currently have a lot of activity in the development of ionic liquid-based electrolytes for these devices. We are also developing polyoxometalate-based redox mediators for batteries and are interested in the solid-state electrochemistry of polyoxometalates.

I am particularly interested in exploring potential collaborations in the areas of electrocatalysis and functional materials.

References

1. D. E. Smith and Darren A. Walsh, The Nature of Proton Shuttling in Protic Ionic Liquid Fuel Cells, *Advanced Energy Materials*, 2019, 9, 1900744.
2. A. Delorme, V. Sans, P. Licence, and D. A. Walsh, Tuning the Reactivity of TEMPO during Electrocatalytic Oxidations in Room-Temperature Ionic Liquids, *ACS Sustainable Chemistry and Engineering*, 2019, 7, 11691-11699.
3. S. Goodwin, D. Smith, J. Gibson, R. G. Jones and D. A. Walsh, Electroanalysis of Neutral Precursors in Protic Ionic Liquids and Synthesis of High-Ionicity Ionic Liquids, *Langmuir*, 2017, 33, 8436-8446.

Haralampos N. Miras

Senior Lecturer (Associate Professor)
University of Glasgow

charalampos.moiras@glasgow.ac.uk

https://www.gla.ac.uk/schools/chemistry/staff/charalamposmoiras/

Research keywords: self-assembly, metal oxides, chalcoxides, mechanistic studies, ESI-MS, catalysis, H_2 evolution.

My research interests are primarily focused on the development of metal oxide/chalcogenide molecule-based materials for energy applications. The current research is focused on the discovery of simple preparation routes to chalcoxide-based molecular and composite functional materials as well as the understanding of fundamental processes in the self-assembly of supramolecular clusters and molecular nanomaterials with modular magnetic, redox, electronic, conductive and catalytic properties.

A synergistic research strand which is being developed in parallel, involves the fundamental understanding, control and design of self-assembled chemical systems. Other recent research projects have investigated the discovery of intermediate reaction structures in an effort to understand the underlying chemistry in the self-assembly of polyoxometalate systems and extraction of crucial mechanistic information utilizing high resolution ESI-MS techniques. I am interested in exploiting novel methodologies such as template effects, investigation of fast kinetics and design of autocatalytic sets for the discovery and design of functional molecular materials.

Possible collaborations with groups interested in mechanistic studies of nano-sized clusters, design of molecule based functional systems and implementation in functional composite materials.

References

[1]. J. McAllister, N. A. G. Bandeira, J. C. McGlynn, A. Y. Ganin, Y.-F. Song, C. Bo, H. N. Miras, *Nature Commun.* **2019**, *10*, 370. "Tuning and mechanistic insights of metal chalcogenide molecular catalysts for the hydrogen-evolution reaction."

[2]. J. W. Purcell, D.-L. Long, E. C. Lee, L. Cronin, H. N. Miras, *Dalton Trans.*, **2018**, *47*, 6283-6287. “Spontaneous formation of a chiral $(Mo_2O_2S_2)^{2+}$-based cluster driven by dimeric $\{Te_2O_6\}$-based templates”

[3]. H. Sartzi, D.-L. Long, S. Sproules, L. Cronin, H. N. Miras, *Chem. Eur. J.* **2018**, *24*, 4399 – 4411. “Directed self-assembly, symmetry breaking, and electronic modulation of metal oxide clusters by pyramidal heteroanions.”

[4]. T. Li, W. Zhang, W. Chen, H. N. Miras, Y.-F. Song, *ChemCatChem*, **2018**, *10(1)*, 188-197. “Modular polyoxometalate-layered double hydroxides as efficient heterogeneous sulfoxidation and epoxidation catalysts.”

[5]. H.-Y. Zang, J.-J. Chen, D. L. Long, L. Cronin, H. N. Miras *Chem. Sci.* **2016**, *7*, 3798-3804. “Assembly of inorganic $[Mo_2S_2O_2]^{2+}$ panels connected by selenite anions to nanoscale chalcogenide–polyoxometalate clusters.”

[6]. H. N. Miras, G. J. T. Cooper, D-L. Long, H. Bögge, A. Müller, C. Streb, L. Cronin, *Science*, **2010**, *327*, 72-74. “Unveiling the Transient Template in the Self-Assembly of a Molecular Oxide Nanowheel”

	Laia Vilà-Nadal
	Lecturer (Assistant Professor) University of Glasgow
	Laia.Vila-Nadal@glasgow.ac.uk
	https://www.gla.ac.uk/schools/chemistry/staff/laiavil/

Research keywords: self-assembly, metal oxide clusters, theory and reaction mechanisms

My goal is to design new oxide materials with applications in energy storage[1], molecular electronics[2], sensing[3] and porous materials[4]. I aim to combine theory and calculations with experimental research by creating interesting molecules, describing their electronic structure, and discovering new properties. I am also interested in using robotics and 3D-printed reactionware with inorganic systems, with the ultimate goal of being able to program the assembly[5] of new materials with properties (e.g. water oxidation catalysis and energy storage materials). I would like to combine those novel synthetic methods with theoretical predictions of some parameters, such as IR, UV-vis, together with real time measurements. That approach would mean achieving an effective navigation through the chemical space, defined by the chemical reactants, and allow for a greater parameter control in the synthesis, and ultimately the digitalization of chemistry.

Possible collaborations: experimental groups interested in self-assembly mechanisms and electronic properties of materials, anyone discover new applications of metal oxide clusters, porous materials.

Reference.

[1] J. -J. Chen, M. D. Symes, L. Cronin, *Nature Chem.*,**2018**, *10*, 1042-1047

[2] C. Busche, L. Vilà-Nadal, J. Yan, H. N. Miras, D. -L. Long, V. P. Georgiev, A. Asenov, R. H. Pedersen, N. Gadegaard, M. M. Mirza, D. J. Paul, J. M. Poblet, L. Cronin, *Nature*, **2014**, *515*, 545-549

[3] C. Zhan, J. M. Cameron, D. Gabb, T. Boyd, R. S. Winter, L. Vilà-Nadal, S. G. Mitchell, S. Glatzel, J. Breternitz, D. H. Gregory, D. -L. Long, A. Macdonell, L. Cronin, *Nat. Commun.*, **2017**, *8*, 14185

[4] L. Vilà-Nadal, L. Cronin, *Nat. Rev. Mat.*, **2017**, *2*, 17054

[5] M. M. Sabi, J. Soriano-López, R. S. Winter, J. -J. Chen, L. Vilà-Nadal, D. -L. Long, J. R. Galan-Mascarós, L. Cronin, *Nat. Cat.*, **2018**,*1*, 208-213

China

Northeast Normal University

	**Yang-Guang Li**
	Professor Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry Northeast Normal University
	liyg658@nenu.edu.cn
	(please insert your homepage address here)

Research keywords: (Polyoxometalates, Synthesis, Energy material, Electrocatalysis)

Polyoxometalates (POMs) are one of unique metal-oxo clusters with fascinating structural topologies, attractive acidic and redox properties and potential applications in catalysis, medicine, nanomaterials, photo-, electro- and magnetic materials. The oxygen-rich surfaces of the POM clusters show active coordination ability with various transition metal ions, lanthanide ions even organic molecules. Thus, it can not only act as molecular building blocks to construct high-dimensional frameworks, but also use as multi-dentate ligands to aggregate TM and/or Ln ions into polynuclear metal clusters. We focus on three research topics: (i) Design and synthesis of POM-based MOFs; (ii) Assembling new polynuclear metal-oxo clusters by the use of lacunary POMs and various TM and Ln ions; (iii) Using various POM-based molecular materials as the platform to fabricate Mo/W-based elecrocatalysts for HER, OER, ORR and CO_2 reduction.

Possible Collaborations: Ken Sakai, Osamu Ishitani, Anna Proust, Elizabeth (Libby) Gibson

Reference:

[1] Y. Y. Ma, C. X. Wu, X. J. Feng, H. Q. Tan*, L. K. Yan, Y. Liu, Z. H. Kang*, E.- B. Wang, Y. G. Li*, *Energy Environ. Sci.,* 2017, 10, 788-798.

[2] X. B. Han, Y. G. Li,* Z. M. Zhang, H. Q. Tan, Y. Lu, E. B. Wang*, *J. Am. Chem. Soc.*, 2015, 137, 5486-5493.

	Hong-Ying Zang
	Professor, Department of Chemistry, Northeast Normal University
	zanghy100@nenu.edu.cn
	(please insert your homepage address here)

Research keywords: (polyoxometalates, ionic-conducting solid electrolytes, proton conducting electrolytes)

Developing new low-cost and efficient proton-conducting materials remains an attractive and challenging task. Polyoxometalates are a type of nanosized redox-active molecules with either rich proton source or other exchangeable cations such as Li$^+$, Na$^+$, K$^+$. We designed and synthesised a series of polyoxometalate-based proton conducting materials. The structure was characterized by single crystal X-ray diffraction, PXRD, FT-IR, TG， solid-state NMR, SEM， TEM and etc. We studied the relationship between the crystal structure and proton conduction of compounds, and studied kinetic process of proton transfer. We have even combined polyoxometalate clusters with polymer matrix to make hybrid membranes which may potentially be used in proton-exchange membrane fuel cells or other energy conversion devices.

Possible Collaborations: Sayaka Uchida, Masahiro Sadakane, Carsten Streb, Ryo Tsunashima

Reference:

[1] Liu, B; Cheng, D. M.; Li, K.; Tan, H. Q.; Zang, H.Y.; Xing, W.; Li, Y. G. *Chem. Sci.* 2019, 10, 556.

[2] Ma, H. P.; Liu B. L.; Li, B.; Li, Y. G.; Tan, H. Q.; Zhang L.; Zang, H. Y.; Zhu, G. S. *J. Am. Chem. Soc*. 2016, 138, 5897.

<table>
<tr><td rowspan="4"></td><td>Li-Kai Yan</td></tr>
<tr><td>Professor, Department of Chemistry, Northeast Normal University</td></tr>
<tr><td>yanlk924@nenu.edu.cn</td></tr>
<tr><td>http://js.nenu.edu.cn/teacher/index.php?zgh=2001900211</td></tr>
</table>

Research keywords: (polyoxometalates, theoretical design, DFT study)

The research activity deals with the application of quantum chemistry computational methods to study the properties and chemical reactivity of polyoxometalates (POMs), and solve chemical problems in close collaboration with experimentalists. Currently, the catalytic mechanisms on water oxidation and carbon dioxide reduction reaction by POMs were explored by using density functional theory (DFT) methods. The catalytic activity of POMs and the reaction pathway were analyzed and further catalyst designs are expected based on the relationship between structures and properties.

Possible Collaborations: Josep M. Poblet, Yong Ding, Craig L. Hill

Reference:

[1] Soriano-López, J.; Musaev, D. G.; Hill, C. L.; Galón-Mascarós, J. R.; Carbó, J. J.; Poblet, J. M. *J. Catal.*, 2017, *350*, 56–63.

[2] Liu, R.-J.; Guangjin Zhang, G.-J.; Cao, H.-B.; Zhang, S.-J.; Xie, Y. B.; Haider, A.; Ulrich Kortz, U.; Chen, B.-H.; Naresh S. Dalal, N.-S.; Zhao, Y.-S.; Zhi, L-J.; Wu, C.-X.; Yan, L.-K.; Su, Z.-M.; Keita, B. *Energy Environ. Sci.*, 2016, *9*, 1012-1023.

	Hua-Qiao Tan
	Associate Professor, Department of Chemistry, Northeast Normal University
	tanhq870@nenu.edu.cn
	(please insert your homepage address here)

Research keywords: (polyoxometalates, electrocatalysis, photocatalysis, Interfacial and surface catalysis)

Electrocatalysis and photocatalysis are considered to be one of the most important and promising technologies for new energy conversion, storage and environmental restoration. The development of high performance catalysts and the study of its catalytic processes and mechanisms are currently hot and challenging topics. Polyoxometalates are one kind of nano metal-oxygen clusters with clear structure and tunable composition. It is an ideal molecular catalytic model and pre-assembly platform. We selected it to design and fabricate a series of highly efficient non-precious metal HER electrocatalysts **CoMoP@C** and **Ni/WC/C** from the atomic or molecular level. In addition, using the reversible multi-electrons and protons storage characteristics of POMs, we realized the regulation of the electron transfer of CO_2 reduction reaction on electrode, and prepared a series of POMs-based environment photocatalysts. These works has verified the important potential application prospects of polyoxometalates in the field of energy and environmental catalysis, and provided an important reference for the development of new POMs-based functional materials.

Possible Collaborations: Graham Newton, Ken Sakai

Reference:

[1] Ma, Y.-Y.; Wu, C.-X.; Feng, X.-J.; Tan, H.-Q.; Yan, L.-K.; Liu, Y.; Kang, Z.-H.; Wang, E.-B.; Li, Y.-G. *Energy Environ. Sci.*, 2017, 10, 788.

[2] Ma, Y.-Y.; Lang, Z.-L.; Yan, L.-K.; Wang, Y.-H.; Tan, H.-Q.; Feng, K.; Xia, Y.-J.; Zhong, J.; Liu, Y.; Kang, Z.-H.; Li, Y.-G. *Energy Environ. Sci.*, 2018, 11, 2114.

[3] Shi, H.-F.; Yu, Y.-C.; Zhang, Y.; Feng, X.-J.; Zhao, X.-Y.; Tan, H.-Q.; Khan, S.-U.; ang, E.-B.; Li, Y.-G. *Appl Catal B-Environ*, 2018, 221, 280.

	Xin-Long Wang
	Professor, Department of Chemistry, Northeast Normal University
	Wangxl824@nenu.edu.cn
	(please insert your homepage address here)

Research keywords: (polyoxometalates, polyoxovanadate-based metal–organic polyhedra, Supramolecular cage)

Polyoxometalte-based nanoscale supramolecular cages are great challenges in the field of polyoxometalates. We designed and synthesised a series of polyoxometalate-based proton conducting materials. We designed and synthesised a series of polyoxometalate-based molecular cage with tetrahedral, octahedral and icosahedral symmetry based on polyoxovanadate-based molecular building blocks. The structures are characterized by single crystal X-ray diffraction, PXRD, FT-IR, TG，ESI-Ms, SEM，TEM and etc. These molecular cages can serve as host frameworks for guests as large as fullerene C60.

Possible Collaborations: Masahiro Sadakane

Reference:

[1] Y. Zhang, H. Gan, C. Qin, X. Wang, Z. Su, M. J. Zaworotko, J. Am. Chem. Soc. 2018, 140, 17365-17368.

[2] Y. Gong, Y. Zhang, C. Qin, C. Sun, X. Wang, Z. Su, Angew. Chem. Int. Ed. 2019, 58, 780-783.

[3] N. Xu, H. Gan, C. Qin, X. Wang, Z. Su, Angew. Chem. Int. Ed. 2019, 58, 4649-4653.

	Weilin Chen
	Professor, Department of Chemistry, Northeast Normal University
	chenwl@nenu.edu.cn
	(please insert your homepage address here)

Research keywords: (polyoxometalates, solar cells, photoelectric property)

Dye-sensitized solar cells (DSSCs) is the third-generation photovoltaic cells developed by Grätzel and O'Regan. It has the characteristics of low cost, simple manufacture process, tunable optical properties, and higher photoelectric conversion efficiency (PCE). With an ever increasing energy crisis, there is an urgent need to develop high efficient, environmentally benign, and energy-saving cell materials. Polyoxometalates (POMs), as a kind of molecular inorganic quasi-semiconductors, are promising candidates being used in different parts of DSSCs due to their excellent photosensitivity, redox, and catalytic properties, as well as relative stability. We try to design and synthesis of serials of new POM compounds, which can be used to enhance the photoelectric conversion efficiency of DSSCs. The properties of POMs, namely, electron acceptor, photosensitivity, redox and catalysis can be efficiently applied in DSSCs.

Possible Collaborations: Graham Newton

Reference:

[1] L. Chen, W. L. Chen*, X. L. Wang*, Y. G. Li, Z. M. Su, E. B. Wang*, *Chem. Soc. Rev.*, 2019, 48, 260-284.

[2] Z. J. Huang, W. J. Luo, L. Ma, M. Z. Yu, X. D. Ren, M. F. He, S. Polen, K. Click, B. Garrett, J. Lu, K. Amine, C. Hadad, W. L. Chen*, A. Asthagiri*, Y. Y. Wu*, *Angew. Chem. Int. Ed.*, 2015, 54, 15181 –15185.

[3] S. S. Xu, Y. H. Wang, Y. Zhao, W. L. Chen*, J. B. Wang, L. F. He, Z. M. Su, E. B. Wang*, Z. H. Kang*, *J. Mater. Chem. A*, 2016, 4, 14025-14032.

[4] L. Chen, W. L. Chen*, H. Q. Tan*, J. S. Li, X. J. Sang, E. B. Wang*, *J. Mater. Chem. A*, 2016, 4, 4125-4133.

[5] C. H. Shan, H. Zhang*, W. L. Chen*, Z. M. Su, E. B. Wang*, *J. Mater. Chem. A*, 2016, 4, 3297-3303.

Germany

Ulm University

Friedrich-Schiller University Jena

	Carsten Streb
	Professor of Inorganic Chemistry, Ulm University Group Leader, Helmholtz Institute Ulm for Electrochemical Energy Storage
	carsten.streb@uni-ulm.de
	www.strebgroup.net

Research keywords: Polyoxometalates; Composites; Energy Sonversion/Storage; Batteries; Photocatalysis; Ionic Liquids; Surface Coatings; Metal Oxide Nanostructures; Carbon Nanostructures

Our research is centred on developing new molecular polyoxometalate-based systems to address grand societal challenges. Our current main focus points are energy technologies and sustainability, particularly solar water splitting[1–3] and new battery technologies.[4,5] In addition, we develop solutions for current challenges such as corrosion protection[6,7] and water purification.[8] The unifying theme is our ambition to bridge the gap between molecular component design and technological materials development. Therefore, our group has built expertise in molecular and materials design, photo- and electrochemistry, catalysis and chemical engineering.

To develop our materials further, we are interested in finding collaboration partners in the fields of materials characterization and simulation, in operando performance characterization as well as new materials design based on functional heterogeneous systems.

References.

[1] W. Luo, J. Hu, H. Diao, B. Schwarz, C. Streb, Y.-F. Song, *Angew. Chem. Int. Ed.* **2017**, *56*, 4941–4944.

[2] D. Gao, R. Liu, J. Biskupek, U. Kaiser, Y.-F. Song, C. Streb, *Angew. Chem. Int. Ed.* **2019**, *58*, 4644–4648.

[3] B. Schwarz, J. Forster, M. K. Goetz, D. Yücel, C. Berger, T. Jacob, C. Streb, *Angew. Chem. Int. Ed.* **2016**, *55*, 6329–6333.

[4] J. Hu, Y. Ji, W. Chen, C. Streb, Y.-F. Song, *Energy Environ. Sci.* **2016**, *9*, 1095–1101.

[5] Y. C. Ji, L. J. Huang, J. Hu, C. Streb, Y.-F. Song, *Energy Environ. Sci.* **2015**, *8*, 776–789.

[6] S. Herrmann, M. Kostrzewa, A. Wierschem, C. Streb, *Angew. Chem. Int. Ed.* **2014**, *53*, 13596–13599.

[7] A. Misra, I. Franco Castillo, D. P. Müller, C. González, S. Eyssautier-Chuine, A. Ziegler, J. M. de la Fuente, S. G. Mitchell, C. Streb, *Angew. Chem. Int. Ed.* **2018**, *57*, 14926–14931.

[8] S. Herrmann, L. De Matteis, J. M. De la Fuente, S. G. Mitchell, C. Streb, *Angew. Chem. Int. Ed.* **2017**, *56*, 1667–1670.

<table>
<tr><td rowspan="4"></td><td>Sven Rau</td></tr>
<tr><td>Professor of Inorganic Chemistry
Ulm University</td></tr>
<tr><td>sven.rau@uni-ulm.de</td></tr>
<tr><td>https://www.uni-ulm.de/en/nawi/nawi-anorg1/</td></tr>
</table>

Research keywords: (Photocatalysis, Artificial Photosynthesis, Water Splitting, Photodynamic Therapy, DSSC's)

We focus our research activities on light driven reactions catalyzed by molecular species. Within this area we work on light driven water splitting, light driven synthesis of NADH and analogoues, photocatalytic CO_2 reduction and application of metal complexes inside living cells for photodynamic therapy.[1-4] The central competence of our research group lies in the ability to synthesize tailored photoredoxactive metal complexes of Ruthenium, Osmium, Rhenium and Iridium which we can characterize with respect to the photochemical and redoxchemical properties in great detail.

To develop our abilities further, we would be interested in structurally versatile POM architectures with redox active components which could be photochemically activated towards changes in structures or other relevant properties. We possess the capability to covalently attach photoactive metal complexes to POM's.

[1] M.G. Pfeffer, B. Schäfer, G. Smolentsev, J. Uhlig, E. Nazarenko, J. Guthmuller, C. Kuhnt, M. Wächtler, B. Dietzek, V. Sundström, S. Rau, *Angew. Chem. Int. Ed.*, **2015**, 54(17), 5044-5048

[2] A. K. Mengele, G. M. Seibold, B. J. Eikmanns, S. Rau, *ChemCatChem*, **2017**, 9, 4369-4376

[3] S. Kaufhold, D. Imanbaew, C. Riehn, S. Rau, *Sustainable Energy Fuels*, **2017**, 1, 2066-2070

[4] S. Chakrabortty, B. K. Agrawalla, A. Stumper, N.M. Vegi, S. Fischer, C. Reichardt, M. Koegler, B. Dietzek, M. Feuring-Buske, C. Buske, S. Rau, T. Weil, *J. Am. Chem. Soc.*, **2017**, 139(6), 2512-2519

Benjamin Dietzek

Professor of Physical Chemistry
Friedrich-Schiller-University Jena
Deputy Director
Leibniz Institute for Photonic Technology, Jena

benjamin.dietzek@uni-jena.de

https://www.ipc.uni-jena.de/AGDietzek.html

Research keywords: Chemistry and physics of electronically excited states; Energy Conversion/Storage; Photoactive Electrodes for Solar Cells and Photoelectrochemical Cells; Photocatalysis; Polyoxometalate-containing molecular dyads and triads; Photoactive drugs

Our group is interested in studying the chemistry and physics of electronically excited states in molecules and materials. A particular focus is on light-induced electron transfer reactions,[1,2] which are key to photoredox catalysis, e.g. solar water splitting,[3,4] or the function of solar cells.[5] We employ a variety of (time-resolved) optical spectroscopic techniques to derive structure-dynamics-function relationships for photoactive molecules and materials. Currently, we are developing ultrafast time-resolved spectroelectrochemistry[6,7] and *in-operando* femtosecond time-resolved spectroscopy to target the excited-state processes in molecular intermediates of complex electron transfer chains.
We are interested in collaborations in the fields of photoactive photosensitizer-polyoxometalate hybrids and functional electrodes for energy conversion and storage to exploit the stimulating interactions between materials' and molecular chemistry and advanced spectroscopic characterization.

Reference.

[1] Luo, Y.; Wächtler, M.; Barthelmes, K.; Winter, A.; Schubert, U.S.; Dietzek, B., Chem. Commun. (2018) 54, 2970-2973.

[2] Schoenweiz, S.; Rommel, S.A.; Kübel, J.; Micheel, M.; Dietzek, B.; Rau, S.; Streb, C., Chem. Eur. J. (2016) 22, 12002-12005.

[3] Pfeffer, M.G.; Kowacs, T.; Wächtler, M.; Guthmuller, J.; Dietzek, B.; Vos, J.G.; Rau, S., Angew. Chem. Int. Ed. (2015) 54, 6627-6631.

[4] Lefebvre, J.F.; Schindler, J.; Traber, P.; Zhang, Y.; Kupfer, S.; Gräfe, S.; Baussanne, I.; Demeunynck, M.; Mouesca, J.M.; Gambarelli, S.; Artero, V.; Dietzek, B.; Chavarot-Kerlidou, M., Chem. Sci. (2018) 9, 4152-4159.

[5] Wahyuono, R.A.; Schulze, B.; Rusu, M.; Wächtler, M.; Dellith, J.; Seyring, M.; Rettenmayr, M.; Plentz, J.; Ignaszak, A.; Schubert, U.S.; Dietzek, B., ChemPlusChem (2016) 81, 1281-1291.

[7] Bold, S.; Zedler, L.; Zhang, Y.; Massin, J.; Artero, V.; Chavarot-Kerlidou, M.; Dietzek, B., Chem. Commun. (2018) 54, 10594-10597.

[8] Zhang, Y.; Traber, P.; Zedler, L.; Kupfer, S.; Gräfe, S.; Schulz, M.; Frey, W.; Karnahl, M.; Dietzek, B., Phys.Chem.Chem.Phys. (2018) 20, 24843-24857.

France

University of Lille

Sorbonne University

Sébastien PAUL

Full Professor
UCCS, Centrale Lille, University of Lille
59650 Villeneuve d'Ascq, France

sebastien.paul@centralelille.fr

http://uccs.univ-lille1.fr/index.php/fr/annuaire/111-paul-sebastien

Research keywords: heterogeneous catalysis, biomass valorization, high-throughput experiments.

Sébastien PAUL is Full Professor at Centrale Lille, a generalist engineer school in the North of France, where he was the head of the Sciences of the Matter department between 2009 and 2016. After his PhD in Chemical Engineering at the University of Technology of Compiègne, France (1996), he was hired by Centrale Lille as an Assistant Professor (1998). From 2004 to 2009 he was at the head of the Chemical Engineering Department, which then became the Sciences of the Matter Department. In 2009, he was nominated Associate Professor and in 2011 Full Professor. His research work is carried out in the Unité de Catalyse et Chimie du Solide (UCCS - UMR CNRS 8181), France, which comprises 300 persons. More particularly he is leading the VAALBIO group (standing for VAlorization of the ALkanes and of compounds issued from the BIOmass).

Sébastien PAUL is also the coordinator of the REALCAT platform ('Advanced High-Throughput Technologies Platform for Biorefineries Catalysts Design' ; 9.4 M€; www.realcat.fr) and the French head of the CNRS French-Japanese International Associate Lab NANOXCAT (2018-2022).

He has supervised or co-supervised 18 PhD, 17 post-docs, is co-author of more than 80 scientific articles (h_{index} =22 – more than 2000 citations), 18 patents, and more than 80 oral communications. He has also co-founded the start-up company TEAMCAT SOLUTIONS in 2015.

He is involved in the development of a large variety of catalytic processes (hydrogenation, oxidation dehydration…) starting from compounds issued from biomass (like glycerol, furfural, sugars, fatty acids, etc.) or light hydrocarbons such as propylene. This research is carried out in the frame of many academic and industrial collaborations.

Most recent papers

- Ni promotion by Fe: what benefits for catalytic hydrogenation?
  D. Shi, R. Wojcieszak, S. Paul, E. Marceau
  Catalysts, 9, 451, (2019)
  DOI:10.3390/catal9050451
- Catalytic decarboxylation of fatty acids to hydrocarbons over non-noble metal catalysts: The state of the art, R. Wojcieszak, A. Kiméné, S. Paul, F. Dumeignil
  J. Chem. Technol. Biotechnol., 94 (3), 658-669, (2019)
  DOI: 10.1002/jctb.5776
- Rational design of selective metal catalysts for alcohol amination with ammonia
  T. Wang, J. Ibañez, K. Wang, L. Fang, M. Sabbe, C. Michel, S. Paul, M. Pera-Titus, P. Sautet
  Nature Catalysis, accepted (2019)
- The Production of 1,3-butadiene from bio-1-butanol over Re-W/γ-Al_2O_3 porous ceramic converter
  A. Fedotov, G. Konstantinov, V. Uvarov, M. Tsodikov, S. Paul, S. Heyte, P. Simon, F. Dumeignil
  Catal. Comm.,128, 105714 (2019)
  DOI: 10.1016/j.catcom.2019.105714
- Fully integrated high-throughput methodology for the study of Ni- and Cu-based supported catalysts for glucose hydrogenation
  F. Ramos, L. Silvester, J. Thuriot-Roukos, S. Heyte, M. Araque Marin, S. Paul, R. Wojcieszak
  Catal. Today, accepted (2019)
- Catalytic dehydration of glycerol to acrolein in a Two-Zone Fluidized-Bed Reactor
  B. Katryniok, R. D. Meléndez, V. Bellière-Baca, P. Rey, F. Dumeignil, N. Fatah, S. Paul
  Front. Chem., 7, 127 (2019)
  DOI: 10.3389/fchem.2019.00127
- Extending catalyst life in glycerol-to-acrolein conversion using non-thermal plasma
  L. Liu, X. P. Ye, B. Katryniok, M. Capron, S. Paul, F. Dumeignil
  Front. Chem., 7, 108 (2019)
  DOI: 10.3389/fchem.2019.00108
- Exploiting the synergetic behavior of Pt-Pd bimetallic catalysts in the selective hydrogenation of glucose and furfural
  P. M. de Souza, L. Silvester, A. G. M. da Silva, C. G. Fernandes, T. S. Rodrigues, S. Paul, P. C. Camargo, R. Wojcieszak
  Catalysts, 9, 132 (2019)
  DOI: 10.3390/catal9020132

- Isoprene formation from isoamyl alcohol in microchannels of a converter modified with nanoscale catalytic iron-chromium-containing systems
  A. S. Fedotov, D. O. Antonov, V. I. Uvarov, M. V. Tsodikov, S. Paul, S. Heyte, F. Dumeignil
  Pet. Chem., 59, 4, 405-411 (2019)
  DOI: 10.1134/S0965544119040066
- Direct amination of 1-octanol with NH3 over Ag-Co/Al_2O_3: Promoting effect of H_2 pressure on the reaction rate
  J. Ibañez, M. Araque-Marin, S. Paul, M. Pera-Titus
  Chem. Eng. J, 358, 1620-1630, (2019)
  DOI: 10.1016/j.cej.2018.10.021
- Glycerol partial oxidation over Pt/Al_2O_3 catalysts under basic and base-free conditions – effect of the particles size
  E. Skrzyńska, A. El Roz, S. Paul, M. Capron, F. Dumeignil
  J. Am. Oil Chem. Soc., 96, 63-74 (2019)
  DOI : 10.1002/aocs.12159
- Bimetallic Fe-Ni/SiO_2 catalysts for furfural hydrogenation: identification of the interplay between Fe and Ni during deposition-precipitation and thermal treatments
  D. Shi, Q. Yang, C. Peterson, A.-F. Lamic-Humblot, J.-S. Girardon, A. Constant-Griboval, L. Stievano, M. T. Sougrati, V. Briois, P. A. J. Bagot, R. Wojcieszak, S. Paul, E. Marceau
  Catal. Today, in press (2019)
  DOI: 10.1016/j.cattod.2018.11.041

Guillaume IZZET

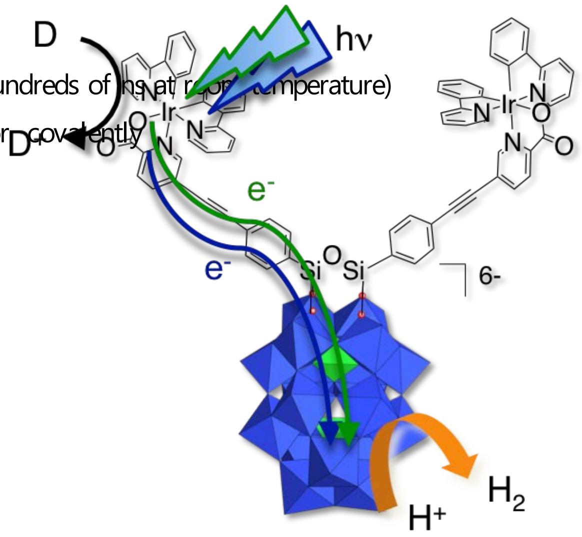
CNRS associate researcher
Sorbonne University
Faculty of Sciences and Engineering
Paris-France

guillaume.izzet@sorbonne-universite.fr

http://www.ipcm.fr/article747.html?lang=en

Research keywords:
Organic-inorganic hybrids based on polyoxometalates, artificial photosynthesis, molecular electronics & photonics, inorganic supramolecular chemistry

My research interests are focused on the design of tailor-made polyoxometalate hybrids for different scopes of application, including artificial photosynthesis.[1-2] I am indeed running a long-term project aiming at elaborating photoactive POM-based hybrids able to perform photocumulative electron transfer.[3-4] Among the hybrids developed, POM-cyclometalated Ir hybrids displayed remarkable photophysical properties.[5-6] The lifetimes of the charge-separated states (ranging from ns to hundreds of ns at room temperature) are the longest reported for covalently bonded photosensitized POMs. Charge photo accumulation and hydrogen photo production was also achieved under steady state photolysis conditions, which makes it a unique system reproducing the different steps of the photosystem (light absorption, charge separation, charge accumulation and multi-electron catalysis).



More recently, I developed a POM-bodipy system.[7] The interest of these compounds lies in the absence of noble metals at in the photoactive antenna as well as in the possibility of subsequently grafting ancillary groups on the organic chromophore in order to develop molecular photocathodes. The photophysical properties of a POM-bodipy compound (studied in collaboration with the group of Dr. Elizabeth Gibson at Newcatle University) showed very rapid electronic injection of bodipy to POM (of the order of 50ps) in agreement with those desired for the development of molecular photocathodes. I also expanded my research interest to POM-based supramolecular assemblies[8-9] and shifted my research topics from covalent functionalization of discrete POMs towards their nanostructuration and integration into functional molecular functional devices.

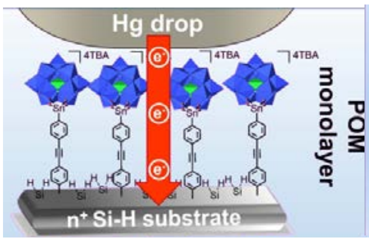
References

1. Proust, A.; Matt, B.; Villanneau, R.; Guillemot, G.; Gouzerh, P.; Izzet, G., Functionalization and post-functionalization: a step towards polyoxometalate-based materials. *Chem. Soc. Rev.* **2012,** *41* (22), 7605-7622.
2. Izzet, G.; Volatron, F.; Proust, A., Tailor-made Covalent Organic-Inorganic Polyoxometalate Hybrids: Versatile Platforms for the Elaboration of Functional Molecular Architectures. *Chem. Rec.* **2017,** (17), 250-266.
3. Bosch-Navarro, C.; Matt, B.; Izzet, G.; Romero-Nieto, C.; Dirian, K.; Raya, A.; Molina, S. I.; Proust, A.; Guldi, D. M.; Marti-Gastaldo, C.; Coronado, E., Charge transfer interactions in self-assembled single walled carbon nanotubes/Dawson-Wells polyoxometalate hybrids. *Chem. Sci.* **2014,** *5* (11), 4346-4354.
4. Matt, B.; Coudret, C.; Viala, C.; Jouvenot, D.; Loiseau, F.; Izzet, G.; Proust, A., Elaboration of Covalently Linked Polyoxometalates with Ruthenium and Pyrene Chromophores and Characteriation of Their Photophysical Properties. *Inorg. Chem.* **2011,** *50* (16), 7761-7768.
5. Matt, B.; Moussa, J.; Chamoreau, L. M.; Afonso, C.; Proust, A.; Amouri, H.; Izzet, G., Elegant Approach to the Synthesis of a Unique Heteroleptic Cyclometalated Iridium(III)-Polyoxometalate Conjugate. *Organometallics* **2012,** *31* (1), 35-38.
6. Matt, B.; Xiang, X.; Kaledin, A. L.; Han, N. N.; Moussa, J.; Amouri, H.; Alves, S.; Hill, C. L.; Lian, T. Q.; Musaev, D. G.; Izzet, G.; Proust, A., Long lived charge separation in iridium(III)-photosensitized polyoxometalates: synthesis, photophysical and computational studies of organometallic-redox tunable oxide assemblies. *Chem. Sci.* **2013,** *4* (4), 1737-1745.
7. Black, F. A.; Jacquart, A.; Toupalas, G.; Alves, S.; Proust, A.; Clark, I. P.; Gibson, E. A.; Izzet, G., Rapid photoinduced charge injection into covalent polyoxometalate-bodipy conjugates. *Chem. Sci.* **2018,** *9* (25), 5578-5584.
8. Izzet, G.; Abécassis, B.; Brouri, D.; Piot, M.; Matt, B.; Serapian, S. A.; Bo, C.; Proust, A., Hierarchical Self-Assembly of Polyoxometalate-Based Hybrids Driven by Metal Coordination and Electrostatic Interactions: From Discrete Supramolecular Species to Dense Monodisperse Nanoparticles. *J. Am. Chem. Soc.* **2016,** *138* (15), 5093-5099.
9. Piot, M.; Abécassis, B.; Brouri, D.; Troufflard, C.; Proust, A.; Izzet, G., Control of the hierarchical self-assembly of polyoxometalate-based metallomacrocycles by redox trigger and solvent composition. *Proc. Natl. Acad. Sci. U. S. A.* **2018,** *115* (36), 8895-8900.

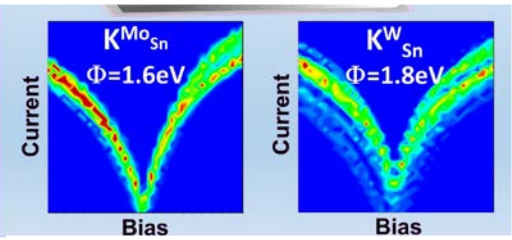
	Pr Anna PROUST
	Sorbonne University Faculty of Sciences and Engineering Paris-France
	(anna.proust@sorbonne-universite.fr)
	http://www.ipcm.fr/article742.html?lang=en

Research keywords: polyoxometalates– organic-inorganic hybrids – nitrogenous ligands – organometallic oxides – electron transfer – solar energy conversion – molecular electronics – surface modification

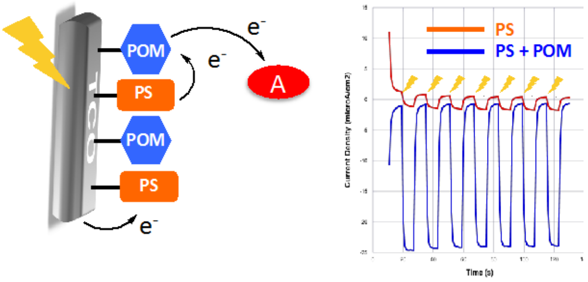
In my career, I have been interested in many aspects of the chemistry of polyometalates (POMs), the use of (multi)-vacant structures as all-inorganic ligands towards extra transition metal cations or organometallic complexes, for application in catalysis (*N*- and *C*-atom transfers, recently CO_2 reduction [1-2]) or molecular magnetism.[3] I have also a special interest in POM-redox properties and the study of related mixed valence species. Finally, I have devoted much efforts to the thorough investigation of POMs functionalization and post-functionalization to form modular and transferable organic-inorganic hybrids.[4-6] My projects are now focusing on POMs as unconventional electro-active molecules to be integrated in functional 2D molecular materials as tunable redox mediators or charge storage nodes. More precisely, for some years I have been studying the controlled deposition of POMs onto electrodes and I am targeting two fields of applications: modified electrodes for non-volatile multi-level digital molecular memories (data storage) and photo-cathodes for artificial photosynthesis.



$[PM_{11}O_{39}\{Sn\mathscr{T}\}]^{4-}$ M = W or Mo



Hg/POM/Si molecular junctions



POM / Photosensitizer /Acceptors for photocathodes

[1] Electro-assisted Reduction of CO_2 to CO and Formaldehyde by the $(TOA)_6[\alpha\text{-}SiW_{11}O_{39}Co(\_)]$ Polyoxometalate M. Girardi, S. Blanchard, S. Griveau, P. Simon, M. Fontecave, F. Bedioui, A. Proust Eur. J. Inorg. Chem., 2015, 3642-3648. DOI: 10.1002/ejic.201500389

[2] Assessing the electrocatalytic properties of the $\{Cp^*Rh(III)\}^{2+}$-Polyoxometalate derivative $[H_2PW_{11}O_{39}\{Rh(III)Cp^*(OH_2)\}]^{3-}$ towards CO_2 reduction M. Girardi, D. Platzer, S. Griveau, F. Bedioui, S. Alves, A. Proust, S. Blanchard Eur. J. Inorg. Chem., 2019, 387-393, DOI : 10.1002/ejic.201800454

[3] - Single ion magnets based on lanthanoid polyoxomolybdate complexes J. Baldovi, Y. Duan, C. J. Bustos, S. Cardona-Serra, P. Gouzerh, R. Villanneau, G. Gontard, J.-M. Clemente-Juan, A. Gaita-Arino, C. Giménez-Saiz, A. Proust and Eugenio Coronado Dalton Trans., 2016, 45, 16653-16660.

[4] Functionalization of polyoxometalates: towards advanced applications in catalysis and materials science A. Proust, R. Thouvenot, P. Gouzerh Chem. Commun., Feature article, 2008, 1837-1852.

[5] Functionalization and post-functionalization a step towards polyoxometalate-based materials A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerh, G. Izzet Chem. Soc. Rev. Themed issue on Polyoxometalates, 2012, 41, 7605-7622. DOI : 10.1039/C2CS35119F

[6] Tailor-made covalent organic-inorganic polyoxometalate hybrids: versatile platforms for the elaboration of functional molecular architectures G. Izzet, F. Volatron, A. Proust, Chem. Record. 2017, 17, 250-266, DOI : 10.1002/tcr.201600092

[7] Electrografting of Diazonium post-functionalized Polyoxometalates: Synthesis, Immobilization and Electron Transfer Characterization from Glassy Carbon C.Rinfray, G. Izzet, J. Pinson, S. Gam Derouich, C. Combellas, F. Kanoufi, A. Proust Chem. Eur. J., 2013,19, 13838-13846. DOI: 10.1002/chem.201302304

[8] Electron Transfer Properties of a Monolayer of Hybrid Polyoxometalates on Silicon F. Volatron, J.-M. Noël, C. Rinfray, P. Decorse, C. Combellas, F. Kanoufi, A. Proust, J. Mater. Chem. C, 2015, 3, 6266-6275. DOI: 10.1039/C5TC00074B

[9] Evidence for Charge Transfer at the Interface between Hybrid Phosphomolybdate and Epitaxial Graphene L. Huder, C. Rinfray, D. Rouchon, A. Benayad, M. Baraket, G. Izzet, F. Lipp-Bregolin, G. Lapertot, L. Dubois, A. Proust, A. G. M. Jansen, F. Duclairoir Langmuir, 2016, 32, 4774-4783. DOI: 10.1021/acs.langmuir.6b00870

[10] Electron Transfer to a Phosphomolybdate Monolayer on Glassy Carbon: Ambivalent Effect of Protonation C. Rinfray, V. Brasiliense, G. Izzet, F. Volatron, S. Alves, C. Combellas, F. Kanoufi, A. Proust Inorg. Chem., 2016, 55, 6929-6937.

[11] Molecular Signature of Polyoxometalates in Electron Transport of Silicon-based Molecular Junctions M. Laurans, K. Dalla Francesca, F. Volatron, G. Izzet, D. Guerin, D. Vuillaume, S. Lenfant, A. Proust Nanoscale, 2018, 10, 1756-17165, DOI: 10.1039/C8NR04946G

[12] Charge transport through molecular junctions based on the redox active $[H_7P_8W_{48}O_{184}]^{33-}$ polyoxometalate processed onto gold surfaces and gold nanodots K. Dalla Francesca, S. Lenfant, M. Laurans, F. Volatron, G. Izzet, V. Humblot, C. Methivier, D. Guerin, A. Proust D. Vuillaume, Nanoscale, 2019, 11, 1863-1878 DOI: 10.1039/C8NR09377F

	Benjamin KATRYNIOK
	Associate Professor UCCS, Centrale Lille, University of Lille 59650 Villeneuve d’Ascq, France
	Benjamin.katryniok@centralelille.fr
	http://uccs.univ-lille1.fr/index.php/fr/annuaire/288-katryniok-benjamin

Research keywords: heterogeneous catalysis, biomass valorization, polyols

Glycerol conversion

One of the most promising valorization ways for glycerol consists on its dehydration to acrolein.[1,2,3] Acrolein is used as an intermediate for the synthesis of DL-methionine as well as for polyacrylate-based polymers. Glycerol dehydration to acrolein can proceed over various solid acid catalysts, such as zeolites, supported inorganic acids or mixed metal oxides (i.e., WO_3). The main drawback of acid catalysis is the deactivation by coking. This issue can be tackled from two strategic angles, either by optimizing the catalysts or from the process side. Concerning the optimization of the catalysts, the crucial parameters are pore diffusion and acid strength. It is well agreed in the literature that medium acid sites and rather large pores are favorable for increased long-term stability. Hence, we focused on silica-supported silicotungstic acid (STA) and optimized the catalytic long-term stability by i) choosing SBA-15 as a support with a tailor-made pore-size of 8 nm and ii) introducing zirconia nanoparticles in SBA-15 in order to moderate the acid-strength of the subsequently supported STA by modulated electronic interactions.[4] These tailor-made properties resulted in outstanding long-term performances with an acrolein yield of 69 % after 24 h with only slight deactivation (initial yield of 74 %) vs. only 24 % for the ZrO_2-free catalyst.

Furthermore, the regeneration of the SBA-15-supported catalytic systems was studied, by burning the carbonaceous species in oxidative atmosphere.[5] Over STA/SBA-15, the regeneration under air led to a significant loss in acrolein yield (30 %) due to the thermal destruction of STA. On the other hand, the catalyst based on zirconia-grafted silica fully recovered its performances due to an increased thermal stability of the active phase, which was ascribed to the strong electronic interaction between STA and zirconia. This specific interaction was also responsible for the slight decrease in the acid strength of the supported STA, just sufficient to avoid coking while still enabling the realization of the glycerol double dehydration reaction. Finally, the cyclic regeneration of the catalysts was performed using periodical switching between a glycerol feed and an air feed with 10 minutes for each cycle. Surprisingly, the catalyst based on zirconia-grafted silica exhibited poor performances (35 % acrolein yield) whereas the catalyst based on bare silica exhibited high and stable performances (74 % yield in acrolein). These results can be understood considering the initial performance of these two catalysts. In fact, while the zirconia-grafted catalyst exhibited outstanding long-term performance, it requires an activation period of about 1 h. In the beginning (0-1 h), the zirconia-grafted catalyst exhibits a poor selectivity to acrolein of no more than 38 %, against 79 % for the catalyst based on bare silica. This type of activation period is well reported for Lewis acid catalysts in the dehydration of glycerol.[6] In fact, Lewis acid sites present on the fraction of zirconia that is not covered by STA first catalyze the selective formation of acetol. Thereby, pseudo-Brønsted sites are formed by hydroxylation, which can then catalyze the selective dehydration to acrolein. As a conclusion, whereas the zirconia-grafted catalyst was adapted to long runs due to a slowed down deactivation and a high thermal stability, the catalyst based on bare silica was adapted to short run/regeneration.

With respect to the possibility of using the catalyst based on bare silica in short reaction / regeneration cycles, we then focused on the process. As aforementioned, the problem of catalyst deactivation can also be tackled from the process side, meaning, i.e., the use of a moving bed reactor or a fluidized bed reactor. Hereby, we focused on a fluidized bed enabling – at the same time – the reaction and the regeneration in the same reaction vessel. The corresponding concept is referred as the two zones fluidized bed reactor (TZFBR).[7] The catalyst is fluidized by means of a pre-heated fluidizing gas (nitrogen or air). Inside the fluidized bed, glycerol can be introduced via a distributor located at the end of a plunging cane. Since glycerol is dragged with the fluidizing gas, the catalytic bed contains two zones. The zone over the glycerol injector is referred as the reaction zone, where the glycerol is catalytically converted to acrolein, and the zone lower than the glycerol distributor is used as a regeneration zone. In this latter part, the deposited carbonaceous species are oxidized with the oxygen co-injected with the carrier gas. With respect to the high cross-mixing of the catalyst in the fluidized bed, the as-regenerated catalyst is constantly exchanged with the catalyst from the reaction zone, allowing thus continuous and efficient regeneration.

The drastic increase in catalyst lifetime motivated us studying the use of “green” acrolein from glycerol dehydration in cascade reactions, and, especially in the ammoxydation of acrolein to acrylonitrile. The synthesis of acrylonitrile from glycerol can proceed either via a direct or an indirect pathway, whereby in the latter case, two independent coupled reactors (tandem reactor concept) must be employed. Although the direct ammoxidation of glycerol appears as advantageous since it requires only one reactor and one catalyst, the subject is discussed controversially in the literature.[8] Thus, we focunsed We focused on the indirect ammoxidation of glycerol using tungsten oxide on titania as a catalyst for the dehydration of glycerol to acrolein and antimony-iron mixed oxide as a catalyst for the ammoxidation of acrolein to acrylonitrile.[9] After optimization of the reaction conditions, a high and stable yield of 40 % was achieved.[10] Surprisingly, this yield in acrylonitrile using the tandem reactor setup was even higher than that theoretically predicted from the performances of the two reactions taken independently (40 % vs. 28 %), suggesting that byproducts from the glycerol dehydration step were also ammoxidized to acrylonitrile. An enlarged study indeed revealed that notably allyl alcohol can give a yield in acrylonitrile as high as 84 % over the antimony-iron oxide catalyst.[11] These results are very promising when considering allyl alcohol as a new platform molecule, which can be actually derived from glycerol in high yields using DODH reaction over a Re-based catalyst with 2-hexanol as H-donor.[12]

Reference

---

[1] Katryniok B, Paul S, Dumeignil F, ACS Catal. 5(8) 1819 (2013).

[2] Katyniok B, Paul S, Bellière-Baca V, Rey P, Dumeignil F, Green Chem. 12(12) 2079 (2010).

[3] Katryniok B, Paul S, Capron M, Dumeignil F, ChemSusChem 2(8) 719 (2009).

[4] Katryniok B, Paul S, Capron M, Lancelot C, Bellière-Baca V, Rey P, Dumeignil F, Green Chem. 12(11) 1992 (2010).

[5] Katryniok B, Paul S, Capron M, Bellière-Baca V, Rey P, Dumeignil F, ChemSusChem 5(7) 1298 (2012).

[6] Alhanash A, Kozhevnikova EF, Kozhevnikov IV, Appl Catal. A 378, 11 (2010).

[7] B. Katryniok, R. Melendez, V. Bellière-Baca, P. Rey, F. Dumeignil, N. Fatah, S. Paul Front. Chem. 7, 127 (2019).

[8] Liebig C, Paul S, Katryniok B, Guillon C, Couturier J-L, Dubois J-L, Dumeignil F, Hoelderich W F. Applied Catalysis B: Environmental 148-149 604-605 (2014).

[9] Liebig C, Paul S, Katryniok B, Guillon C, Couturier J-L, Dubois J-L, Dumeignil F, Hölderich WF, Appl. Catal. B. Env. 148-149, 604 (2014).

[10] Liebig C, Paul S, Katryniok B, Guillon C, Couturier J-L, Dubois J-L, Dumeignil F, Hölderich WF, Appl. Catal. B. Env. 123-133, 170 (2013).

[11] Guillon C, Liebig C, Paul S, Mamede AS, Hölderih WF, Dumeignil F, Katryniok B, Green Chem. 15, 3015 (2013).

[12] Y. Kon, M. Araque, T. Nakashima, S. Paul, F. Dumeignil, B. Katryniok Chemistry Select 9864. (2017).

Japan

Hiroshima University

Nihon University

Kyoto University

Kanagawa University

Kanazawa University

The University of Tokyo

Mitsubishi Chemical Corporation

Tokai University

Kwansei Gakuin University

Kochi University

Chubu University

Kyushu University

Tokyo Institute of Technology

Wakayama University

Yamaguchi University

The National Institute of Advanced Industrial Science and Technology (AIST)

Japan Synchrotron Radiation Research Institute (JASRI)

Nippon Inorganic Colour & Chemical Co., LTD

	Masahiro Sadakane
	Professor Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University
	sadakane09@hiroshima-u.ac.jp
	https://home.hiroshima-u.ac.jp/catalche/

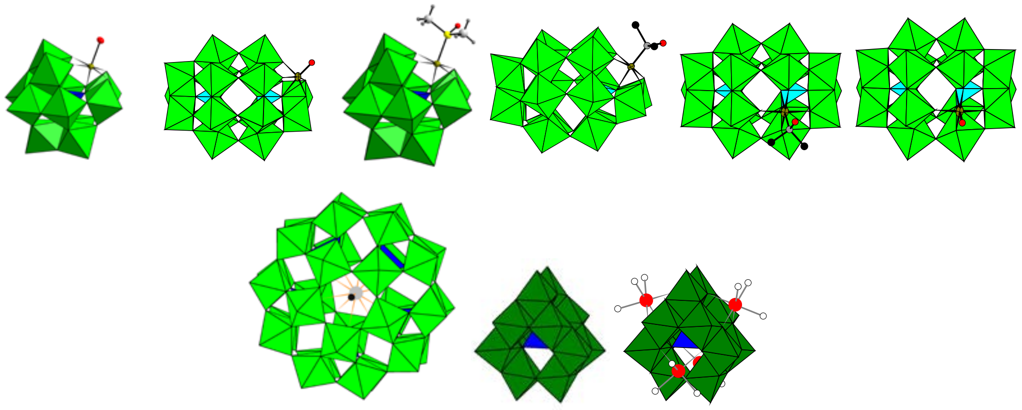
Research keyword: Ruthenium containing POM; Preyssler-type POM; ε-Keggin based metal oxide; High-resolution ESI-MS; Water oxidation catalyst; Porous Materials.

Ruthenium containing POM. We investigate methods to prepare mono-Ru substituted heteropolytungstates such as $[XW_{11}O_{39}Ru(H_2O)]^{n-}$ (X = P, Si, or Ge) and α_1- or α_2-$[P_2W_{17}O_{39}Ru(H_2O)]^{7-}$, and their derivatives [1]. These show multi-electron redox properties and are active oxidation catalysts for several reaction including water oxidation.

Preyssler-type POM. We found that acid property of Preyssler-type heteropolyacid, $H_{15-n}[P_5W_{30}O_{110}M^{n+}]$ is higher than that of Keggin-type phosphotungstic acid. We investigate synthesis of new Preyssler-type derivatives [2].

ε-Keggin based metal oxide. We are interested in synthesis of porous all inorganic molybdenum oxides by connecting epsilon-Keggin heteropolymolybdate and application as adsorption materials and catalysts [3].

High-resolution ESI-MS. We use high-resolution ESI-MS with an accuracy of 3 ppm [1,2,4]. We can measure your samples.



[1] a) *Dalton Trans*. **2016**, *45*, 3715. b) *Inorg. Chem*. **2014**, *53*, 3526. [2] a) *ACS Omega*, **2018**, *3*, 2363. b) *Inorg. Chem*. **2016**, *55*, 11583. [3] a) *Inorg. Chem*. **2017**, *56*, 2043. b) *Inorg. Chem*. **2014**, *53*, 7309. [4] a) *Eur. J. Inorg. Chem*. **2019**, ??. b) *Inorg. Chem*. **2017**, *56*, 8759. c) *Inorg. Chem*. **2016**, *55*, 8292.

	Tomoji OZEKI
	Professor College of Humanities and Sciences, Nihon University
	ozeki@chs.nihon-u.ac.jp
	https://dep.chs.nihon-u.ac.jp/chemistry/ozeki1.html

Research keywords: Crystallography, intermolecular interactions, hydrogen bonds, crystal design.

We are interested in the intermolecular interactions involving polyoxometalates. Main topics include (i) solid-state and solution structures of hydrogen-bond assisted polyoxometalate aggregates, (ii) crystal design of nano-scale polyoxometalates, and (iii) design of molecular composites consisting of polyoxometalates and silver ethynide clusters.

(i) Hydrogen-bond assisted polyoxometalate aggregates: We showed that protonated decavanadates, $H_nV_{10}O_{28}^{(6-n)-}$, exhibit cation- and solvent-dependent various hydrogen-bonding aggregates in crystals [1] and such aggregates are transferred into the solution phase [2]. Multinuclear NMR and small angle X-ray scattering (SAXS) demonstrated that hydrogen-bonded oligomer formations are reversible and depends on the nature of the solvents.

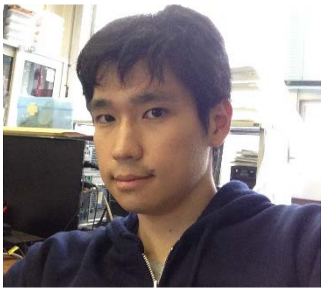
(ii) Crystal design of nano-scale polyoxometalates: Controlled crystallization of wheel-type and spherical nano-scale polyoxometalates allowed us to reveal their nuclearity growth and crystallization mechanisms [3] and to construct crystals with huge water channel with the diameter of 3 nm [4]. Analyses of these structures were made possible by the synchrotron X-ray diffraction.

(iii) Design of molecular composites: We are extending our study to the intermolecular interactions of polyoxometalates with other kinds of cluster compounds. With the combination of silver ethynide clusters, we have demonstrated that the molecular composites can rationally designed by controlling the structures of the polyoxometalates [5, 6].

Possible collaborations

We can offer our state-of-the art synchrotron single-crystal X-ray diffraction experiences. Also, any collaborations using our compounds are welcome.

References. [1] Nakamura & Ozeki, *J. Chem. Soc., Dalton Trans., 2001*, 472. [2] Kojima, Antonio & Ozeki, *J. Am. Chem. Soc., 2011*, **133**, 7248. [3] Shishido & Ozeki, *J. Am. Chem. Soc., 2008*, **130**, 10588. [4] Saito & Ozeki, *Dalton Trans., 2012*, **41**, 9846. [5] Kurasawa, Arisaka & Ozeki, *Inorg. Chem., 2015*, **54**, 1650. [6] Tamari, Ono, Hashimoto & Ozeki, *Dalton Trans. 2015*, **44**, 19056.

	Kenji Ohashi Department of Chemistry, College of Humanities and Sciences, Nihon University oohashi.kenji@nihon-u.ac.jp

Research keywords: Synthesis, X-ray crystal structure analysis, Photochemistry

My research is to synthesize new compounds containing polyoxometalate and to explore their photofunctional materials having unique photophysical properties and photochemical reactions. We recently reported the photocatalytic hydrogen evolution mechanism using a polyoxometalate—silver ethynide composite cluster, $[\{Ag_{12}(C\equiv C^{t}Bu)_7(H_2O)(NMP)_3\}_2\{Ni_4(NMP)_2(PW_9O_{34})_2\}]$ (NMP = *N*-methyl-2-pyrrolidone), in the presence of a photoredox catalyst and a reductant. The photocatalytic reaction was achieved that H_2 production increases with time after exposure to visible light and 4.6 μmol H_2 was obtained after 3 h of irradiation. This was higher than that of $[Ni_4(H_2O)(PW_9O_{34})_2]^{10-}$ or Ag^+ as the hydrogen evolution catalyst. The color of solution containing the composite cluster changed from yellow to reddish brown which derived from the plasmonic absorption of Ag(0) nanoparticles. UV-vis, IR, SEM/EDX, and Powder X-ray diffraction of the sample after photoirradiation revealed that the composite cluster was reduced to the compound comprising Ag(0) nanoparticles and polyoxometalates by the one electron reduced species of the Ir complex (Figure 1). The polyoxometalate-Ag(0) nanoparticles efficiently drives the H_2 production reaction as the catalyst. In the future, we plan to develop the photofunctional polyoxometalate materials.

I have technics for research concerning X-ray structure analysis and photochemistry except for synthesis of polyoxometalates, so it is possible to collaborate from this point of view.

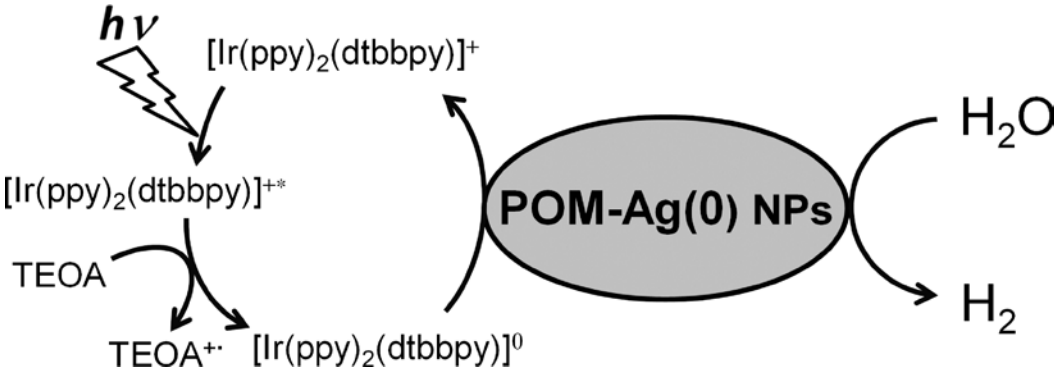
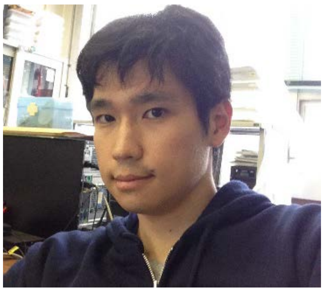


Figure 1 The schematic illustration of photocatalytic hydrogen evolution reaction.



Kenji Ohashi
Department of Chemistry, College of Humanities and Sciences, Nihon University
oohashi.kenji@nihon-u.ac.jp

Syntheses and crystal structures of composite clusters comprising Weakley-type polyoxometalate and silver(I) ethynide complexes

We prepared a series of composite clusters (**Ag-M$_{\mathbf{POM}}$**) comprising sandwich-type polyoxometalates ($[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) and silver ethynide complexes. These compounds were obtained as crystals which were precipitated from *N*-methyl-2-pyrrolidone solutions containing $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, $AgC\equiv C^{t}Bu$, and CF_3SO_3Ag. Single-crystal X-ray structure analyses revealed that composite clusters, $[\{Ag_{12}(C\equiv C^{t}Bu)_7(C_5H_9NO)_3\}_2\{M_4(C_5H_9NO)_2(PW_9O_{34})_2\}]$ (**Figure 1**), consist of two $[Ag_{12}(C\equiv C^{t}Bu)_7(C_5H_9NO)_3]^{5+}$ and one $[M_4(C_5H_9NO)_2(PW_9O_{34})_2]^{10-}$. These composite clusters have the same molecular structure, and as the result, their obtained crystals were the same crystalline form. Different crystalline form of the composite cluster comprising Ag(I) ethynide complexes and polyoxometalate also appeared as the impurity. It is difficult to isolate only the desired compounds, because these composite clusters also give different crystalline. However, the problem was resolved by adding a crystal of the same crystalline and it was obtained the desired crystalline compounds. We successfully obtained, isolated and characterized the composite clusters comprising Weakley-type polyoxometalate and silver(I) ethynide complexes.

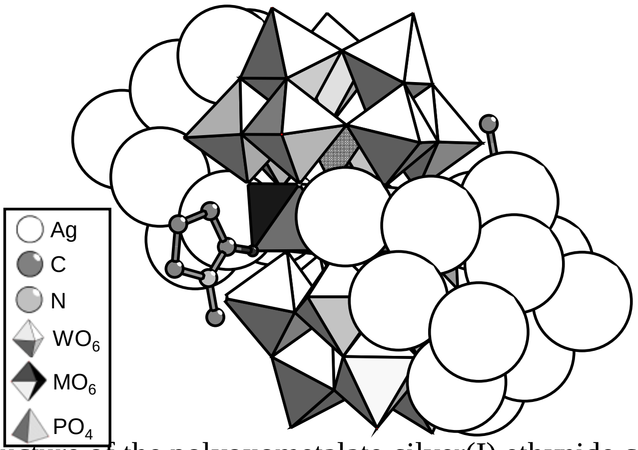


Figure 1. Structure of the polyoxometalate-silver(I) ethynide composite cluster. Organic ligands on silver clusters are omitted for clarity.

Acknowledgments
This work was supported by JSPS Core-to-Core Program.

Osamu Tomita

Graduate School of Engineering, Kyoto University
Assistant Professor

tomita.osamu.6s@kyoto-u.ac.jp

http://www.ehcc.kyoto-u.ac.jp/eh41/home/abe/index.html

Research keywords: Redox mediator, Transition metal-substituted polyoxometalate, Two-step water splitting, Hydrogen production

Transition Metal substituted Polyoxometalate as an Effective Shuttle Redox Mediator in Z-scheme Water Splitting into H2 and O2 under Visible Light

Water splitting systems based on two-step photoexcitation, so-called Z-scheme systems, have recently been developed and proven as a promising approach to harvesting a wider range of visible light,[1,2] because the water splitting reaction is separated into two parts, i.e., H_2- and O_2-evolving systems. Although the introduction of Z-scheme systems enables us to employ various visible-light responsive photocatalysts, the choice of redox has been limited to simple ion couples such as IO_3^-/I^- and Fe^{3+}/Fe^{2+}. This is mainly due to the problems with mismatching redox potentials and/or irreversibility presented by other materials. Therefore the suitable properties of redox couple for Z-scheme water splitting is still unclear in this research field, and also the development of new redox couples is strongly desired in order to widen the available choice of Z-scheme photocatalyst materials and achieve highly efficient water splitting under visible light. Here, we have paid attention to the use of transition metal-substituted-polyoxometalates,[3] most of which are known to exhibit reversible redox behavior derived from valence differences between the incorporated transition metals, as effective shuttle redox mediators. We have recently reported a new Z-scheme water splitting system using a polyoxometalate as a redox mediator; the use of a Mn-substituted silicotungstate or Mo-substituted one ($K_6[SiW_{11}O_{39}Mn^{II}(H_2O)]$ or $K_4[SiW_{11}O_{40}Mo^{VI}]$) with appropriate photocatalysts enabled a stoichiometric evolution of H_2 and O_2 under visible light.[4, 5]

In the present study, various kinds of metal substituted polyoxometalate will be prepared and employed as redox mediator between the two photocatalysts in order to obtain the knowledge toward the preparation of redox mediator with suitable properties for efficient Z-scheme water splitting.

1. R. Abe, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 1000.
2. A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253.
3. M. Sadakane, E. Steckhan, *J. Mol. Catal. A* **1996**, *114*, 221.
4. K. Tsuji, O. Tomita, M. Higashi, R. Abe, *ChemSusChem,* **2016**, *9*, 2201.
5. Y. Iwase, O. Tomita, M. Higashi, R. Abe, *J. Photochem. Photobiol. A: Photochem.* **2018**, *356*, 347.

	Ishikawa Satoshi
	Faculty of Engineering, Department of Material and Life Chemistry, Research associate
	sishikawa@kanagawa-u.ac.jp
	http://apchem2.kanagawa-u.ac.jp/uedalab/

Research keywords: High dimensionally structured materials, polyoxometalate, building units, selective oxidations

Synthesis of high dimensionally structured mixed metal oxide by an assembly of structural units from giant polyoxometalate

Heterogeneous catalytic selective oxidation of hydrocarbons is an attractive reaction since the reaction produces valuable chemicals such as alcohols, aldehydes, acids, etc. Recently, the selective catalytic oxidation of light alkanes has attracted much attention due to the shale gas revolution and to the concern about petroleum. However, success in the reactions has been limited so far despite tremendous efforts. This is due to the difficulty of the catalytic selective oxidations since multiple catalytic functions, such as an adsorption and desorption properties of substrates and products (acid-base property), an activation property of substrate and oxygen (redox property), etc, are required to achieve the reaction. It appears that the following two functions have to be implemented into the solid-state oxidation catalysts; (1) special catalysis field effective for capturing and activating substrates, and (2) active site isolation effective for generating active oxygen species from molecular oxygen and for limiting the reaction between the activated substrates and the oxygen species to a desired reaction direction. The catalyst having the above two functions should be ideal, but it is difficult to synthesize such the catalyst. For synthesizing such the catalyst, a material synthetic methodology should be developed to introduce the above functions in a crystal structure in a designable manner. It is noted that the desired materials will be inevitably complex and be a high dimensionally structured. Here, the presenter introduced the ideas to create new class of solid state catalysts active for selective oxidations. The catalysts are created based on the assembly of structural units provided by specific polyoxometalates and forms high dimensional structure containing multiple catalytic sites.

Reference. [1] Ishikawa, S.; Zhang, Z.; Ueda, W. *ACS Catal.* **2018**, *8*, 2935-2943. [2] Ishikawa, S.; Ueda, W. *Catal. Sci. Technol.* **2016**, *6*, 617-629.

	Yuji Kikukawa
	Associate professor Faculty of Chemistry, Institute of Science and Engineering, Kanazawa University
	kikukawa@se.kanazawa-u.ac.jp
	http://chem.s.kanazawa-u.ac.jp/inorg/

Research keywords: Vanadium, Structure Transformation, Catalysis, Host-Guest System

Host-Guest Chemistry of Dodecavanadate

Vanadium-based polyoxometalates show structural versatility. Especially, square pyramidal VO_5-based polyoxometalates tend to form a spherical-type structure that allows guest anions to be accepted at the center. A particularly intriguing example is that of a bowl-type polyoxometate framework, $[V_{12}O_{32}]^{4-}$ (**V12**), which possesses a 4.4 Å wide cavity entrance surrounded by eight oxygen atoms. In the cavity, an electron-rich group or an anion can be stabilized via unique electrostatic interactions.[1] By removing a guest moiety, a guest free type of **V12** (**V12-free**) with a bottom-flipped bowl structure was prepared. [2] The prohibition of the guest-removal was demonstrated with a chloride-incorporated **V12** (**V12(Cl)**). By adding acid and base, the reversible structure transformation of **V12(Cl)** with opened form and closed form. The incorporated chloride was preserved in the closed form even in the presence of a silver cation, while the chloride in opened form was removed as AgCl.[3]

Our group is good at synthesis of novel POMs, structure transformation, rational modification of POMs and their characterization. We can offer several kinds of POMs and can collaborate on the adsorption IR measurements, the single crystal and powder XRD analysis, and the catalyst activity evaluation.

Reference. [1] (a) S. Kuwajima, Y. Ikinobu, D. Watanabe, Y. Kikukawa, Y. Hayashi, A. Yagasaki, *ACS Omega*, **2017**, *2*, 268. (b) S. Kuwajima, Y. Kikukawa, Y. Hayashi, *Chem. Asian J.*, **2017**, *12*, 1909. [2] (a) Y. Kikukawa, K. Seto, S. Uchida, S. Kuwajima, Y. Hayashi, *Angew. Chem. Int. Ed.* **2018**, *57*, 16051. (b) Y. Kikukawa, H. Kitajima, Y. Hayashi, *Dalton Trans*. **2019**, *48*, 7138. (a) Y. Inoue, Y. Kikukawa, S. Kuwajima, Y. Hayashi, *Dalton Trans*., **2016**, *45*, 7563. (b) S. Kuwajima, Y. Arai, H. Kitajima, Y. Kikukawa, Y. Hayashi, *Acta Crystallogr*. **2018**, *C74*, 1295.

	Kazuya Yamaguchi
	Professor, Department of Applied Chemistry, School of Engineering, The University of Tokyo
	kyama@appchem.t.u-tokyo.ac.jp
	http://park.itc.u-tokyo.ac.jp/mizuno/english/index.html

	Kosuke Suzuki
	Associate Professor, Department of Applied Chemistry, School of Engineering, The University of Tokyo
	ksuzuki@appchem.t.u-tokyo.ac.jp
	http://park.itc.u-tokyo.ac.jp/mizuno/english/index.html

	Tomohiro Yabe
	Research Associate, Department of Applied Chemistry, School of Engineering, The University of Tokyo
	tyabe@appchem.t.u-tokyo.ac.jp
	http://park.itc.u-tokyo.ac.jp/mizuno/english/index.html

Research keywords: Inorganic Synthesis, Homogeneous Catalysis, Heterogeneous Catalysis, Photocatalysis, Oxidation Reaction, Magnetism

Abstract

In order to realize highly efficient, selective, and energy-saving chemical reactions, it is necessary to develop next-generation catalyst technology that can design structures and functions at the atomic level. Polyoxometalates (POMs) are molecular metal oxide clusters that exhibit various physical properties, such as magnetism, dielectric properties, electrical conductivity, optical properties, and catalytic properties. We have developed the precise synthesis method of POMs in organic solvents (Fig. 1). In particular, we didn't utilized lacunary POMs as simple "templates" but utilized them in concert with the introduced metal atoms, and we explored new methodologies in the design of POMs catalysts, including the development of visible-light-responsive photoredox catalysis and highly efficient concerted catalysis.[1–5] We are also studying on heterogeneous POM catalysts for gas-phase reactions of hydrocarbons.

Precise synthesis of POMs: We have developed the precise synthesis method of POMs by controlling the reactivity of lacunary POMs by changing the protonation state and/or using protecting groups, such as alcohol and pyridine, in organic solvents. We synthesized metal oxide nanoclusters by introducing various transition metals, main group elements, and rare earth metals in one step into the lacunary POMs.[3] We also succeeded in developing a new synthesis method to introduce different metals sequentially in the controlled metal arrangement.[4] In particular, by controlling the magnetic anisotropy and spin states of metal oxide nanoclusters, we have developed materials exhibiting excellent single ion magnet properties and single molecule magnet properties.

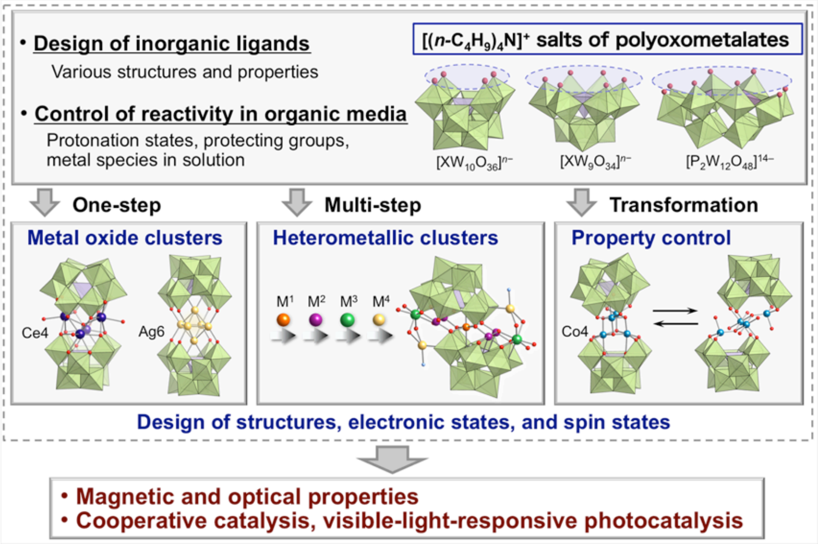


Fig. 1 Development of the precise synthesis method of POMs for functional materials and catalysis.

Development of high-performance POM catalysis: Based on our synthetic methods, we developed a high-performance POM catalysis for various liquid phase reactions. For example, we developed visible-light-responsive redox catalysis for functional group transformations by controlling the electronic states of POMs using the introduced metal atoms and organic substrates (Fig. 2).[5]

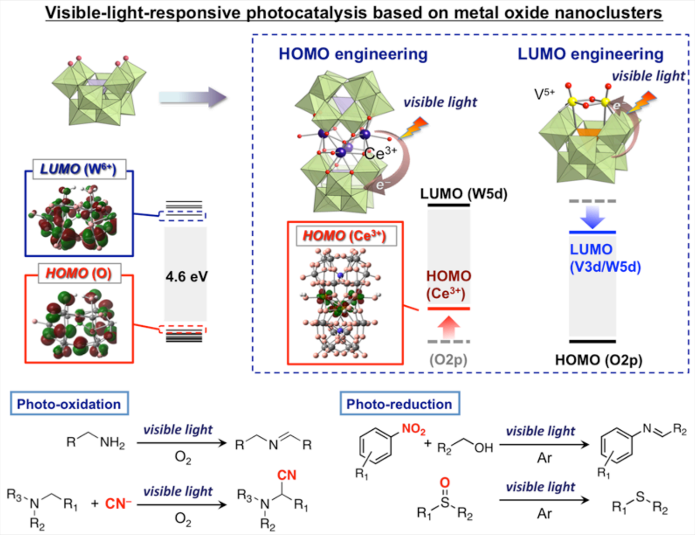


Fig. 2 Visible-light-responsive POM photocatalysis for selective functional group transformations.

Possible collaborations:

- Liquid-phase (photo)catalytic reactions
- Gas-phase catalytic reactions for conversion of hydrocarbons
- Synthesis of various polyoxotungstates and polyoxomolybdates
- Synthesis of solid catalysts based on polyoxometalates

References:

1. Suzuki, K.; Mizuno, N.; Yamaguchi, K. *ACS Catal.* **2018**, *8*, 10809 (review article of POM photocatalysis).
2. (a) Li, C.; Mizuno, N.; Yamaguchi, K.; Suzuki, K. *J. Am. Chem. Soc.* **2019**, *141*, 7687. (b) Minato, T.; Suzuki, K.; Yamaguchi, K.; Mizuno, N. *Angew. Chem. Int. Ed.* **2016**, *55*, 9630.
3. (a) Suzuki, K.; Sato, R.; Mizuno, N. *Chem. Sci.* **2013**, *4*, 596. (b) Suzuki, K.; Kikukawa, Y.; Uchida, S.; Tokoro, H.; Imoto, K.; Ohkoshi, S.; Mizuno, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 1597. (c) Kikukawa, Y.; Suzuki, K.; Sugawa, M.; Hirano, T.; Kamata, K.; Yamaguchi, K.; Mizuno, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 3686.
4. (a) Minato, T.; Ohata, Y.; Ishii, K.; Yamaguchi, K.; Mizuno, N.; Suzuki, K. *J. Mater. Chem. C* **2019**, in press. (b) Minato, T.; Suzuki, K.; Ohata, Y.; Yamaguchi, K.; Mizuno, N. *Chem. Commun.* **2017**, *53*, 7533.
5. (a) Li, C.; Suzuki, K.; Mizuno, N.; Yamaguchi, K. *Chem. Commun.* **2018**, *54*, 7127. (b) Suzuki, K.; Jeong, J.; Yamaguchi, K.; Mizuno, N. *Chem. Asian J.* **2015**, *10*, 144. (c) Suzuki, K.; Tang, F.; Kikukawa, Y.; Yamaguchi, K.; Mizuno, N. *Angew. Chem. Int. Ed.* **2014**, *53*, 5356.

	Wataru Ueda
	Faculty of Engineering, Department of Material and Life Chemistry, Professor
	uedaw@kanagawa-u.ac.jp
	http://apchem2.kanagawa-u.ac.jp/uedalab/index.html
	Satoshi Ishikawa
	Faculty of Engineering, Department of Material and Life Chemistry, Research associate
	sishikawa@kanagawa-u.ac.jp
	http://apchem2.kanagawa-u.ac.jp/uedalab/index.html

Research keywords: All inorganic microporous materials, Building units, Transition metals, Selective oxidations

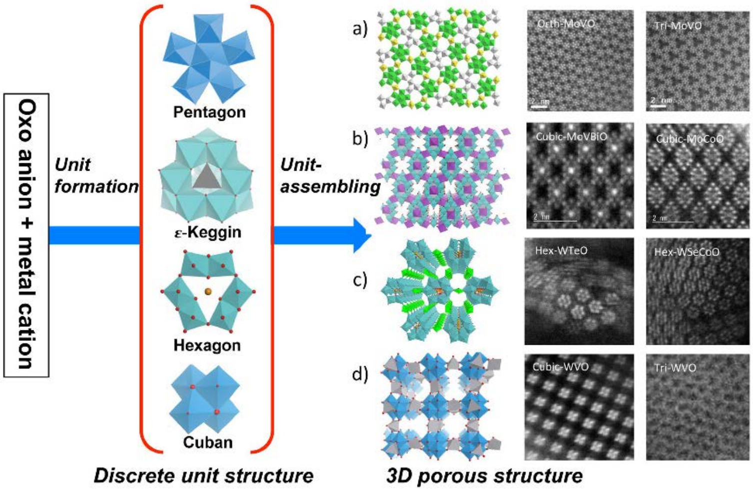


Figure. Four distinct metal oxides with 3D porous structures derived from discrete unit assembling. a) - d) are structure models and HAADF-STEM

We have been synthesizing microporous materials with all inorganic manner using transition metals as main constituents and developing them for various applications such as catalysts, selective adsorptions, cathode material for lithium ion battery, etc. For the synthesis of these materials, we create various polyoxometalates (POMs) in the precursor solution using various transition metals. These POMs are as sembled for each other with appropriate inorganic linker under an appropriate hydrothermal condition to form highly organized crystalline materials. Thus obtained materials form micropores in the crystal structure like as zeolites and show attractive properties based on its highly organized crystalline structure and the redox natures.

- **Possible collaborations**

Selective oxidation, adsorption

- **Reference.** [1] Ishikawa, S.; Zhang, Z.; Ueda, W. *ACS Catal.* **2018**, *8*, 2935-2943. [2] Zhang, Z.; Ueda, W, *et al. Nat. Commn.* **2018**, *6*, 7731.

	Hiroki Miyaoka
	Associate professor Natural Science Center for Basic Research and Development, Hiroshima University
	miyaoka@h2.hiroshima-u.ac.jp
	https://home.hiroshima-u.ac.jp/hydrogen/

Research keywords: Hydrogen, Hydrogen storage, Hydrogen production, Material conversion, Oxide

Our research group focus on material conversion techniques such as hydrogen production, hydrogen storage, and nitride synthesis by chemical reactions using light elements such as lithium (Li), sodium (Na), and magnesium (Mg). To understand essential properties of the above materials, all the synthesis and analyses process can be performed without exposing materials into air by using glove box and special experimental systems. The representative works are introduced below.

Magnesium hydride (MgH_2) is attractive hydrogen storage material because of its high gravimetric hydrogenation capacity, 7.6 wt.%. However, the improvement of reaction kinetics for hydrogen absorption and desorption required. To operate the reactions, higher temperature than 300 °C is generally required as thermal activation. Niobium oxide (Nb_2O_5) is an excellent catalyst to drastically improve the reaction kinetics of Mg1, 2). However, the detailed mechanism is not understood yet. Recently, research on the catalytic mechanism of functional oxides such as Nb_2O_5 proceeds as collaboration work in "Center for Functional Nano Oxide" in Hiroshima University, and novel knowledges are obtained.

In addition to the above research, thermochemical hydrogen production via chemical reactions based on redox reactions of sodium (Na/NaO_x)3) and nitride synthesis by pseudo catalytic process based on the reactions of lithium (Li) alloys4).

Reference

[1] N. Hanada, T. Ichikawa, S. Hino and H. Fujii, Remarkable improvement of hydrogen sorption kinetics in magnesium catalyzed with Nb_2O_5, J. Alloys Compd. 420, 46-49, 2006.

[2] T. Kimura, H. Miyaoka, T. Ichikawa and Y. Kojima, Hydrogen absorption of catalyzed magnesium below room temperature, Int. J. Hydrogen Energy 38, 13728-13733, 2013.

[3] H. Miyaoka, T. Ichikawa, N. Nakamura and Y. Kojima, Low-temperature water-splitting by sodium redox reaction, Int. J. Hydrogen Energy 37, 17709-17714, 2012.

[4] S. Yamaguchi, T. Ichikawa, Y. Wang, Y. Nakagawa, S. Isobe, Y. Kojima and H. Miyaoka, Nitrogen Dissociation via Reaction with Lithium Alloys, ACS Omega 2, 1081-1088, 2017.

Wataru Ninomiya

Chief Scientist, PhD
MMA Group, Chemicals Laboratory, Hiroshima R&D Centre,
Development Division, Mitsubishi Chemical Corporation

ninomiya.wataru.me@m-chemical.co.jp

https://www.m-chemical.co.jp/

Research keywords: Heteropolyacid catalysts, Oxidation, Methyl methacrylate, Industrial process

Heteropolyacids show excellent acidic and redox properties and play a very important role as a catalyst even in industrial processes. There are some examples for industrial heteropolyacid catalysts such as an oxidation catalyst of methacrolein to methacrylic acid, a hydration catalyst of light olefins to corresponding alcohols and a polymerisation catalyst of tetrahydrofuran.[1] Mitsubishi Chemical Corporation (MCC) has been focusing on the development of heteropolyacid-based oxidation catalysts of methacrolein to methacrylic acid in a gas phase for several decades. The catalytic reaction is recognised as a part of one of methyl methacrylate (MMA) processes, i.e. C_4 Direct Oxidation (C_4-DO) process starting from isobutylene oxidation. The global production capacity of MMA is ca. 4,500 kte/y and ca. 30% of it is produced by C_4-DO process. At the present time, MCC group occupies ca. 36% of the global capacity and operates MMA business as the leading company.

Our aim is to develop the industrial catalyst for methacrolein oxidation based on Keggin-type PMo heteropolyacid showing high selectivity and extended catalyst life. The development of highly performing catalysts can assure the competitiveness of our C_4-DO MMA process. We have also been underpinning science of heteropolyacid-based compounds from micro to macro structure by using various characterisation techniques.

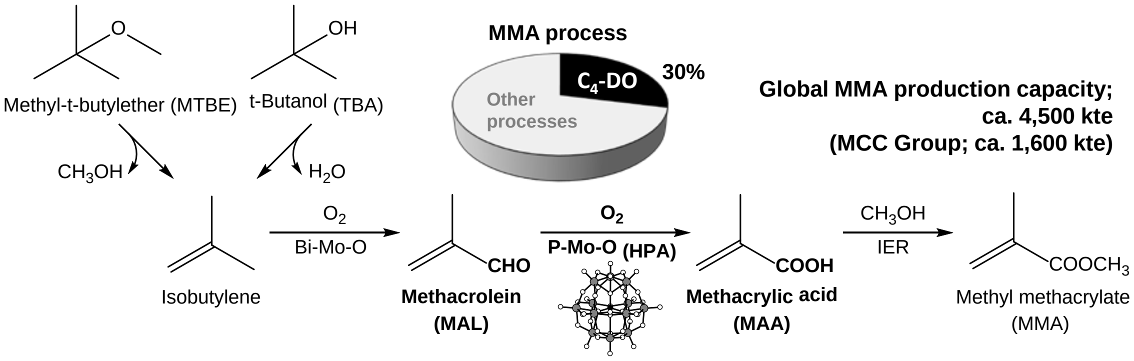
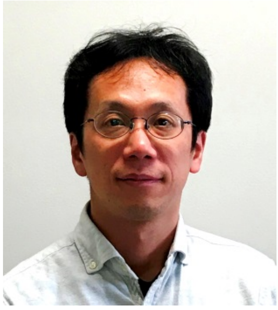


Figure 1 C_4 Direct Oxidation (C_4-DO) process for MMA production and its production capacity

Reference

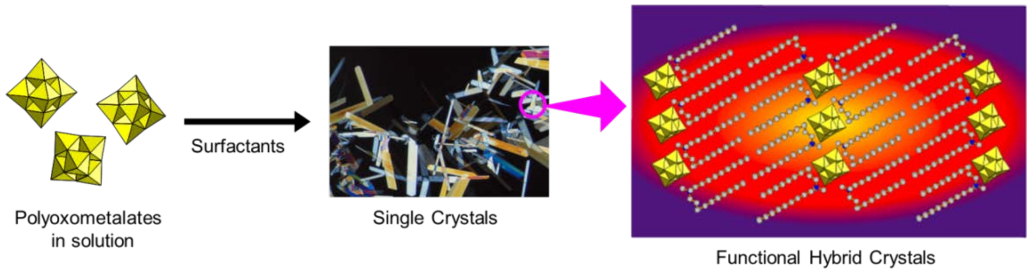
1. M. Misono and N. Nojiri, *Appl. Catal.* 60 (1990) 1−30

	Takeru Ito
	Professor Department of Chemistry, School of Science, Tokai University, Hiratsuka, Japan
	takeito@keyaki.cc.u-tokai.ac.jp
	http://www.sc.u-tokai.ac.jp/

Research keywords: inorganic-organic; hybrid material; single crystal; surfactant; polyoxometalate

Hybridization of inorganic and organic components have potential for the construction of functionalized crystalline materials. We can expect synergy of the merits derived from the both components, and polyoxometalate cluster anions are promising candidates as inorganic components to construct functional hybrid materials. We have synthesized several polyoxometalate hybrids by using structure-directing surfactants to obtain inorganic-organic functional crystals [1]. The polyoxometalate-surfactant hybrid crystals enable fine tuning of the structure and function by changing the combination of polyoxometalate anion and surfactant cation. Some of them exhibit electronic and proton conductivities [2]. The introduction of metal cations into such hybrid crystals can provide functions such as ionic conductivity and ion-exchanging property [3]. Recently, newly designed polymerizable ionic-liquids have been successfully hybridized with Keggin-type anions and octamolybdates to form inorganic-organic hybrid monomers and polymers [4]. Possible collaboration will be to provide our hybrid materials for the evaluation of ionic conductivity, chromic property, and redox catalysis.

Inorganic-Organic Hybrid Crystals Constructed from Surfactants and Polyoxometalates



Reference. [1] T. Ito, *Crystals*, **6**, 24 (2016). [2] S. Otobe, Y. Kiyota, S. Magira, T. Misawa, K. Fujio, H. Naruke, S. Uchida, T. Ito, *Eur. J. Inorg. Chem.*, 442-447 (2019). [3] J. Kobayashi, T. Misawa, C. Umeda, T. Isono, S. Ono, H. Naruke, Y. Okamura, S. Koguchi, M. Higuchi, Y. Nagase, T. Ito, *CrystEngComm*, **21**, 629-636 (2019). [4] T. Ito, S. Otobe, T. Oda, T. Kojima, S. Ono, M. Watanabe, Y. Kiyota, T. Misawa, S. Koguchi, M. Higuchi, M. Kawano, Y. Nagase, *Polymers*, **9**, 290 (2017).

	Hirofumi Yoshikawa
	Associate Professor, Kwansei Gakuin University
	yoshikawah@kwansei.ac.jp
	http://www.kg-nanotech.jp/yoshikawa/en/

Research keywords: polyoxometalate, rechargeable battery, X-ray absorption fine structure analysis

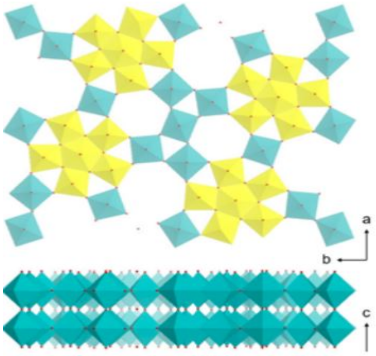


Figure 1. Structure of Mo-V-Bi oxide

Development of high-performance rechargeable batteries is one of the most important research issues. Recently, to achieve both high capacity and fast charging/discharging, we proposed a new type of lithium battery, the molecular cluster battery (MCB), in which the cathode active materials are polynuclear metal complexes. We have used a Keggin-type polyoxometalate (POM) cluster, $[PMo_{12}O_{40}]^{3-}$, as a cathode-active material, and this lithium battery showed a large capacity of ca. 270 mAh/g, which is higher than those of the usual lithium ion batteries (ca. 150 mAh/g), due to its super-reduction during discharge process [1]. These results suggested that POMs can be promising cathode active materials.

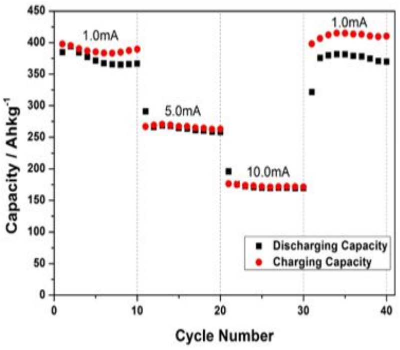


Figure 2. Rate capability of Mo-V-Bi oxide

Herein, we report the performance and reaction mechanism of Li batteries using porous polyoxometalate, Mo-V-Bi oxide ($Mo_{30.5}V_{9.5}Bi_{1.1}O_{112}$, see Fig. 1), which has a robust three-dimensional MoV oxide framework [2]. This battery exhibited a large capacity of ca. 376 mA h/g, which was maintained and decreased only a little after 40 cycles in a voltage range between 4.0 and 1.5 V. They also showed a high rate capability (see Fig. 2) indicating an excellent structural stability, reversibility, long-term property and very high-speed Li migration during battery reactions. X-ray absorption fine structure (XAFS) analyses revealed that more than 70 electrons redox occurred during this battery reaction, which can explain the large experimental specific capacity.

As mentioned above, we can measure the battery performances of various polyoxometalate materials as collaborative works.

[1] H. Yoshikawa et al, *J. Am. Chem. Soc.*, **2012**, 134, 4918.

[2] H. Yoshikawa et al, *ACS Applied Materials & Interfaces*, **2017**, 9, 26052.

Atsushi Yagasaki

Professor of Chemistry
Kwansei Gakuin University

yagasaki@kwansei.ac.jp

https://sci-tech.ksc.kwansei.ac.jp/en/faculty/atsushi-yagasaki/

Research keywords: molecular oxide, solution chemistry

The focus of our research is on extending the chemistry of molecular oxides. We call the compounds “molecular oxides” and not “polyoxometalates” because the word polyoxometalate indicates the compound is anionic and contains metals. Polyoxometalates have compositions and structures reminiscent of oxides. However, there are potentialy many such compounds that are neither anionic nor contain any metallic elements [1]. Octaantimonate, $[Sb_8O_{12}(OH)_{20}]^{4-}$, is one such example that has been isolated and structurally characterized in our effort to expand the chemistry of molecular oxides [2]. During the course of our study, we have also discovered the tetrahedral tellurate anion, TeO_4^{2-}, and nitroxyl anion, NO^- [3, 4]. The TeO_4^{2-} anion is stable in non-aqueous solutions, although people thought Te atom is too large to form a stable tetrahedral oxoanion. The NO^- anion had been deemed too reactive to be isolated in the condensed phase. We still do not have much to report on the “cationic front”, but had some minor success there and obtained a mixed valent, tetra-nuclear Pt compound [5]. Another branch of our study is the reaction of molecular oxides with small molecules. It was during the study of the reaction of $[Nb_{10}O_{28}]^{6-}$ with NO that we unexpectedly obtained $[Nb_{20}O_{54}]^{8-}$ [6]. Later, we confirmed this dimerization is reversible and stoichiometric [7]. In the study of the reaction of $[IMo_6O_{24}]^{5-}$, we found this anionic molecular oxide undergoes protonation/deprotonation reversibly and reacts with methanol with a very selective manner [8]. Lately, we are interested in the hydrogen-bonded oligomers of molybdoplatinate and just found that the $[H_9(PtMo_6O_{24})_2]^{7-}$ dimer [9] stays intact in solution.

Obviously, solution chemistry is our strong point. We could undertake some joint studies if any of the participants are interested in the solution chemistry of their compound.

References. [1]…Baes, C. F., Jr., Mesmer, R. *The Hydrolysis of Cations*; Wiley: New York, 1976.
[2] Nakano, H.; Ozawa, Y.; Yagasaki, A., *J. Am. Chem. Soc.*, **1995**, *117*, 12007-12008.
[3] Konaka, S.; Ozawa, Y.; Yagasaki, A., *Inorg. Chem.*, **2008**, *47*, 1244-1245.
[4] Kawanami, N.; Ozeki, T.; Yagasaki, A., *J. Am. Chem. Soc.*, **2000**, *122*, 1239-1240.
[5] Noro, K.; Ozawa, Y.; Taguchi, M.; Yagasaki, A., *Chem. Commun.*, **2002**, 1770-1771.
[6] Maekawa, M.; Ozawa, Y.; Yagasaki, A., *Inorg. Chem.*, **2006**, *45*, 9608-9609.
[7] Matsumoto, M.; Ozawa, Y.; Yagasaki, A., *Polyhedron*, **2010**, *29*, 2196-2201.
[8] Honda, D.; Ikegami, S.; Inoue, T.; Ozeki, T.; Yagasaki, A., *Inorg. Chem.*, **2007**, *46*, 1464-1470.
[9] Ikegami, S.; Kani, K.; Ozeki, T.; Yagasaki, Y., *Chem. Commun.*, **2010**, 785-787.

	Prof. Tadaharu Ueda
	Department of Marine Resource Science Faculty of Agriculture and Marine Science Kochi University
	chuji@kochi-u.ac.jp
	http://www.cc.kochi-u.ac.jp/~chuji/eng/index_eng.htm

Research keywords: Sulfur-centered polyoxometalates; electrochemistry; redox mechanism; sensors

We have tried to prepare novel polyoxometalates (POMs) by using different hetero ions. A lot of novel metal-substituted tungstosulphates and organo-phosphates incorporating POMs have been prepared, isolated and characterized with various synthetic techniques [1]. We have focused on electrochemistry of POMs, which is very rich since many electrons transferred processes occur without decomposition. Although many of POMs have been applied to important fields such as battery and water splitting based on their electrochemical properties, there are still unclear aspects on the voltammetric behavior. We have tried to elucidate the detailed voltammetric behavior with simulation of cyclic voltammograms with a help of NMR, ESR and the other measurements [2]. In addition, we have been interested in new (electrochemical) sensors with POMs. Formation reaction and reduction of POMs have been used for spectrophotometric determination of phosphorus and silica, so called molybdenum blue method and molybdenum yellow method [3]. Achievements of our studies on POMs improved sensitivity in molybdenum blue method. In addition, electrochemical method of antioxidant capacity has been developed to measure more easily than the reported methods: ORAC and DPPH [4]. I hope to make new collaborations with anyone who is interested in the development of catalytic reactions and sensors with my POMs and/or electrochemistry of your POMs.

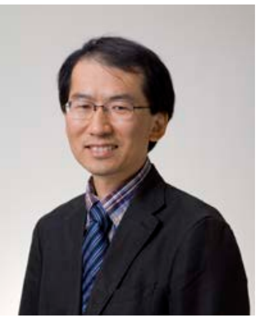
References

[1] (a) *Inorg. Chem. Commun.*, 2013, **38**, 123-126; (b) *Inorg. Chem.*, 2014, **53**, 4891-4898.

[2] (a) *Dalton Trans.*, 2010, **39**, 7364-7373; (b) *Dalton Trans.*, 2014, **43**, 5462-5473; (c) *Dalton Trans*, 2015, **44**, 11660-11668; (d) *J. Electroanal. Chem.*, 2016, **779**, 67-74; (e) *Electrochim. Acta*, 2016, **201**, 45-56; (f) *Inorg. Chem.*, 2017, **56**, 3990-4001; (g)T. Ueda, *ChemElectroChem*, 2018, **5**, 823-838.

[3] (a) *Anal. Sci.*, 2001, **17**, 1431-1435; (b) *Anal. Sci.*, 2011, **27**, 1043-1047.

[4] (a) *Anal. Sci.*, 2016, **32**, 825-830; (b) *J. Electroanal. Chem.*, 2018, **828**, 102-107.

<table>
<tr><td rowspan="4"></td><td>Yoshihito Hayashi</td></tr>
<tr><td>Professor, Chemistry Chair
Chemistry Department, Graduate School of Natural Science and Technology, Kanazawa University,
Kakuma, Kanazawa, 920-1192, Japan</td></tr>
<tr><td>hayashi@se.kanazawa-u.ac.jp</td></tr>
<tr><td>chem.kanazawa-u.ac.jp/inorg/index.html</td></tr>
</table>

Research keywords: Vanadium, Polyoxovanadates

Research abstract: The element vanadium has named after the Scandinavian goddness, the god of beauty, love and maturity, *Vanadis*. It is avandant in seawater and important in industry as catalyst, an additive to steel and new materials. In chemistry, the solution containing vanadium complexes is known to exhibit a spectrum of a beautiful color. This is because of the possible versatile oxidation states in vanadium as well as the coordination spheres. Especially, a square-pyramidal five-coordination mode is particularly important only in vanadium. Polyoxovanadates, may offer a new way to further expand the boundary of coordination chemistry for inorganic complexes featuring a part of metal oxide structures. Because of the complexity of the oxides, it is difficult to elucidate the structure and property relationships. Investigating the reactivity and physical properties by modifying the oxide structures in a systematic manner is challenging to test the hypothesis of a postulated mechanism. Polyoxovanadates have a molecular structure comparable to vanadium oxides and we try to establish the way to control its frameworks for a particular application.

Possible collaboration: Fundamental chemistry of polyoxovanadates is our focus with the classification based on their structural building units and we can offer diverse range of new polyoxovanadates almost exclusively from our lab, including the structural types of bowls, tubes, spheres, blocks, rings with 3d-transition elements as the heteroatom, in crystal quality.

Reference.

[1] Y. Hayashi, *Bull. Jpn. Soc. Coord. Chem*., **66**, 12–25, (2015).
[2] Y. Hayashi, *Coord. Chem. Rev*., **255**, 2270–2280 (2011).

<table>
<tr><td rowspan="4"></td><td>Sayaka UCHIDA</td></tr>
<tr><td>Associate Professor, Dr.
School of Arts and Sciences, The University of Tokyo
Komaba 3-8-1, Meguro-ku, Tokyo 153-8902, Japan</td></tr>
<tr><td>csayaka@mail.ecc.u-tokyo.ac.jp</td></tr>
<tr><td>http://park.itc.u-tokyo.ac.jp/suchida/</td></tr>
</table>

Research Keywords: Ionic Crystals, Porous Materials, Redox Chemistry, Cation-Exchange and Uptake, Proton Conduction, Heterogeneous Catalysis.

Abstract: We are interested in synthesizing functional porous ionic crystals based on POMs, which are different from conventional porous crystalline materials such as zeolites and MOFs. Some of our recent works are summarized as follows: **I**. Redox-active ionic crystals containing redox-active POMs as constituents show cooperative migration of electrons with metal ions in the porous structure (so called cation-coupled electron-transfer (CCET) in relation to proton-coupled electron-transfer (PCET)). We have recently reported selective adsorption of Cs$^+$ from aqueous solutions[1,2] and formation of small mixed-valence luminescent silver clusters[3]. **II**. POMs can efficiently transport protons because of the relatively low surface charge density, while application has been limited by the low structural stability. In order to solve this problem, POMs are hybridized with polymers especially with those containing amine group, which serves as protonation sites. The crystalline hybrids show high proton conductivity due to the extended hydrogen-bonding network and segmental motion of the polymers.[4,5] **III**. Ionic components create strong electrostatic fields at internal surfaces of the pores, which are suitable for accommodation and stabilization of polar guests and cationic intermediates. We have reported structure-function relationships in conventional acid-type reactions such as pinacol rearrangement[6] and biomass-related[7] reactions.

Possible Collaborations: Please provide us with POMs and counter cations, which may show interesting properties as components of ionic crystals!! We have experience in characterization of solids (elemental analysis, solid state NMR, *in situ* powder XRD, gas and vapor adsorption studies, impedance measurements, catalytic reactions, etc).

References: I. **Redox-active ionic crystals**: (1) S. Seino, R. Kawahara, Y. Ogasawara, N. Mizuno, S. Uchida, *Angew. Chem. Int. Ed.*, 55, 3987 (2016). (2) S. Hitose, S. Uchida, *Inorg. Chem*., 57, 4833 (2018). (3) S. Uchida, T. Okunaga, Y. Harada, S. Magira, Y. Noda, T. Mizuno, T. Tachikawa, *Nanoscale*, 11, 5460 (2019). **II**. **Proton Conduction**: (4) T. Iwano, S. Miyazawa, R. Osuga, J. N. Kondo, K. Honjo, T. Kitao, T. Uemura, S. Uchida, *Communs. Chem.*, Article number: 9 (2019). (5) K. Niinomi, S. Miyazawa, M. Hibino, N. Mizuno, S. Uchida, *Inorg. Chem.*, 56, 15187 (2017). **III**. **Heterogeneous Catalysis**: (6) R. Kawahara, R. Osuga, J. N. Kondo, N. Mizuno, S. Uchida, *Dalton Trans.*, 46, 3105 (2017). (7) T. Yamada, K. Kamata, E. Hayashi, M. Hara, S. Uchida, *ChemCatChem*, in press. DOI: 10.1002/cctc.201900614.

Eri ISHIKAWA

Associate Professor
Department of Applied Chemistry, College of Engineering,
Chubu University

eishikawa@isc.chubu.ac.jp

https://www.chubu.ac.jp/english/faculty/index.html

Research keywords: X-ray structural analysis, Multinuclear NMR spectroscopy, Electrospray ionization mass spectrometry (ESI-MS), Isothermal titration calorimetry (ITC)

Polyoxometalates, characterized by high reactivity and functionality, have attracted considerable attention for their application in the fields of catalysis, material science, and medicine. We have explored the behavior of polyoxometalate ion in solution with the help of multinuclear NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and isothermal titration calorimetry (ITC). Our present research interests are development of environmentally friendly oxidation catalysis. Now we have many trials to improve their catalytic activity and elucidate their process based on solution chemistry. Our recent results related to solution chemistry are as follows:

Cyclooctene epoxidation catalyzed by vanadium-substituted Lindqvist-type polyoxotungstate:[1] Tetrabutylammonium salts of Lindqvist $[VW_5O_{19}]^{3-}$ significantly promotes cyclooctene epoxidation with H_2O_2 in CH_3CN at 30 °C. The catalytic processes are discussed based on the UV/Vis, ESI-MS, ^{51}V NMR, and ^{183}W NMR spectra. Analysis of ESI-MS showed that the $[VW_5O_{19}]^{3-}$ anion retained a Lindqvist-type structure, and the multiple peroxidations occurred at both the V and W sites during epoxidation. With the synergistic effects provided by the W(peroxo) sites, the V(peroxo) site plays a catalytically active role in both epoxidation and H_2O_2 decomposition.

The formation of elliptical $\{Mo_{134}La_{10}\}$ ring by incorporating La^{3+} into the inner ring of circler $\{Mo_{142}(CH_3CO_2)_5(C_2H_5CO_2)\}$ ring in aqueous solution:[2] Modification of the Mo-ring from circle to ellipsoid was investigated using the ITC and ^{139}La NMR spectrometry coupled with the results of X-ray structural analysis of circler $\{Mo_{142}(CH_3CO_2)_5(C_2H_5CO_2)\}$ ring and elliptical $\{Mo_{134}La_{10}\}$ ring. $\{Mo_{142}(CH_3CO_2)_5(C_2H_5CO_2)\}$ ring comprised of carboxylate-coordinated $\{Mo_2\}$ linkers and six defect pockets in inner ring. Regarding the endothermic reaction of $[La^{3+}]/\{Mo_{142}\}=6/1$ with $\Delta H=22$ kJ•mol^{-1}, $\Delta S=172$ J•K^{-1}•mol^{-1}, and $K=9.9\times10^4$ M^{-1} at 293 K, the results of ITC conclude that the coordination of the defect pockets to La^{3+} precedes the replacement of the $\{Mo_2\}$ linkers with La^{3+}.

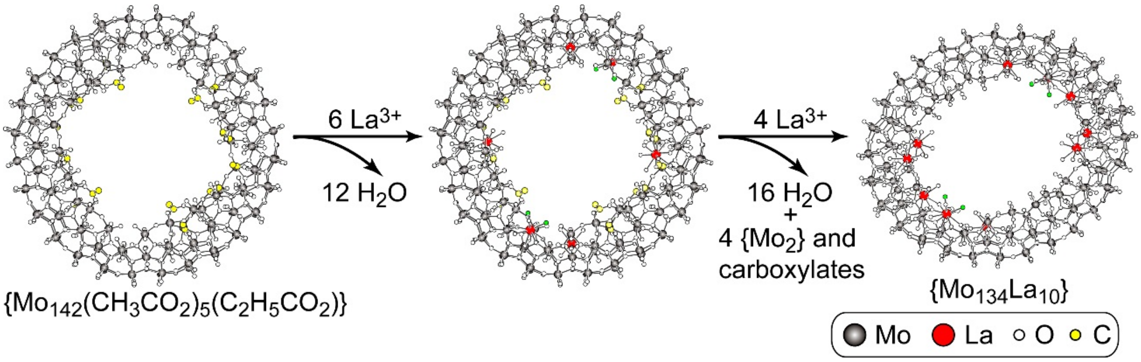


Figure. Two step of the coordination of $\{Mo_{142}(CH_3CO_2)_5(C_2H_5CO_2)\}$ to La^{3+} in aqueous solutions.

Catalytic hydrolysis of Adenosine Triphosphate (ATP) by polyoxomolybdate:[3, 4] Polyoxomolybdate ion, both of $[Mo_7O_{24}]^{3-}$ and $[H_2Mo^V{}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$, show the antitumor activity against human gastric cancer and pancreatic cancer. These polyoxomolybdates also promote ATP hydrolysis to adenosine diphosphate (ADP). $[H_2Mo^V{}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$ is a photoreduction product obtained through the photolysis of $[Mo_7O_{24}]^{3-}$ at the pH range 5 to 7. The processes of ATP hydrolysis catalyzed by these polyoxomolybdates were investigated with ^{31}P NMR spectrometry, ESI-MS and ITC. $[Mo_7O_{24}]^{3-}$ ion exhibits high catalytic activity at the pH range 2 to 6. The resulst of ^{31}P NMR spectra and ITC suggested that ATP was decomposed through the formation of the ATP-molybdate complexes isostructural with $[(PO_4)_2Mo_5O_{15}]^{6-}$ and $[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ as intermediates. The ATP hydrolysis in the presence of $[H_2Mo^V{}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$ proceeds catalytically at the pH range 5 to 7.5. The $[H_2Mo^V{}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$ interacts weakly with ATP. The results of ESI-MS measurements suggest that ATP hydrolysis proceed retaining structure of $[H_2Mo^V{}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$ anion.

Reference

[1] E. Ishikawa, D. Kihara, Y. Togawa, and C. Ookawa, *Eur. J. Inorg. Chem.* **2019**, 402–409.
[2] E. Ishikawa, Y. Yano, and T. Yamase, *Materials* **2010**, *3*, 64-75.
[3] E. Ishikawa, and T. Yamase, *Eur. J. Inorg. Chem.* **2013**, 1917–1925.
[4] E. Ishikawa, and T. Yamase, *J. Inorg. Biochem.* **2006**, *100*, 344-350.

	Takehiko Gotoh
	Assistant Professor Hiroshima University
	tgoto@hiroshima-u.ac.jp
	https://home.hiroshima-u.ac.jp/polymer3/en/index.html

Research keywords: Polymer gel

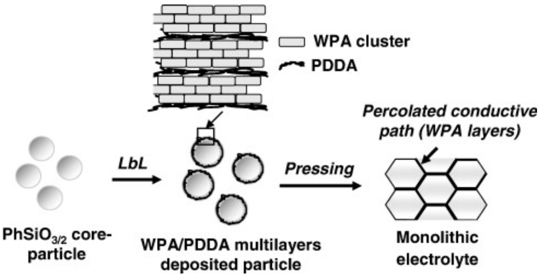
My Research: The development of novel stimuli-responsive polymer and gel, and their application to the novel reaction and separation processes.

Possible collaborations: I can make separation, reaction, and storage field made by hydrogel that consists of ionic polymer and aqueous solution. The field gives easy separation method from the liquid and optimal reaction conditions to catalysts. I would like to collaborate with those who are looking for stable reaction field for POM preparation or reaction.

	Kiyofumi Katagiri
	Professor Department of Applied Chemistry Hiroshima University
	kktgr@hiroshima-u.ac.jp
	http://home.hiroshima-u.ac.jp/inumaru

Research keywords: Organic-inorganic hybrid materials, Sol-gel method, Hydrothermal process, Supramolecular assembly, Layer-by-layer assembly, Bioinspired materials, Structurally colored materials, Nanoparticles, Theranostic materials, Photocatalysts, Mixed-anion compounds, Metal oxynitrides, etc.

Heteropolyacid-based composites for proton conductors



Thermally and chemically stable phenylsilsesquioxane ($PhSiO_{3/2}$) particles were prepared by sol–gel process, and ultra-thin layers of oppositely charged poly(diallyldimethylammonium chloride) (PDDA) and dodecatungstophosphoric acid (WPA) were alternately deposited on the negative-charged $PhSiO_{3/2}$ particles via layer-by-layer (LbL) assembly technique. Hygroscopic property of WPA was remarkably reduced owing to the formation of PDDA/WPA complex. The amount of WPA adsorbed on $PhSiO_{3/2}$ particles was estimated to be ~ 0.03 (g/g $PhSiO_{3/2}$). Transparent and monolithic pellet can be obtained from the resultant core–shell particles by pressing. Proton conductivity of WPA-deposited samples increased about 4 orders of magnitude compared with unmodified samples, and reached to about 10^{-4} S/cm at 80 °C and 80% relative humidity [1].

Next, cesium salts of Cs_2SO_4, Cs_2CO_3 and $CsHSO_4$ and WPA were mechanically milled to synthesize chemically durable WPA composites. The X-ray diffraction patterns of composites suggested the formation of partially substituted $Cs_xH_{3-x}PW_{12}O_{40}$ composites after milling at 720 rpm for 10 min. Proton conductivities under both humidified and dry conditions of the resultant composites markedly improved. The proton conductivities strongly depended on the type of cesium salt. The hydrogen bonding distance L in the frame structures of the composites was estimated from the ^{1}H-isotropic chemical shift. The proton conductivities in dry conditions of $WPA \cdot 6H_2O$ and the composites were strongly represented to L [2].

[1] Y. Daiko, K. Katagiri, K. Shimoike, M. Sakai, A. Matsuda, *Solid State Ionics,* **178**, 621 (2007).

[2] Y. Daiko, H. Takagi, K. Katagiri, H. Muto, M. Sakai, A. Matsuda, *Solid State Ionics*, **179**, 1174 (2008).

	Takashi Ogi
	Associate Professor Department of Chemical Engineering, Fuculty of Engineering, Hiroshima University,
	Ogit@hiroshima-u.ac.jp
	https://takashiogi.amebaownd.com/

Research keywords: Particle and process engineering, Nanostructured particles, Nanoparticle, Resource recovery, Spray process, Aerosol process, Porous structure, Hollow structure, Core-shell structure.

Our group focuses on i) synthesis and functionalization of nanoparticle [1,2], ii) synthesis of nanostructured particles for energy, environmental, food, and medical applications [3], and (iii) resource recovery and recycling [4,5], for building a sustainable society. Regarding (iii), we developed a facile method for tungsten ion removal using lysine for the development of an environmentally friendly and sustainable recycling technique (Fig. 1). Lysine addition to the tungsten solution achieved 100% tungsten removal within 5 min, as a white lysine-tungsten precipitate. Electrospray ionization mass spectrometry analyses of the tungsten and lysine mixed solutions showed that lysine promoted dehydration condensation reactions of anionic tungsten species such as HWO^{4-} and $W_6O_{19}{}^{2-}$ through the electrostatic interactions between positively charged lysine and negatively charged tungsten ions. Calcination of the lysine–tungsten precipitate produced tungsten oxide powder of high purity (99.6%) because the lysine is completely decomposed. This facile and useful metal removal method can be used for polyoxometalates of other metals such as molybdenum, tantalum, and niobium.

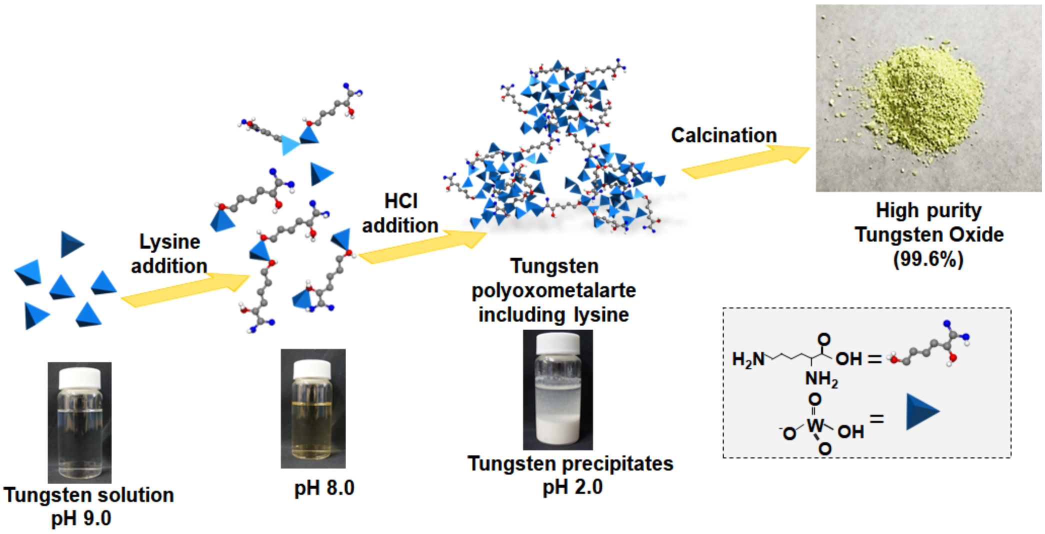
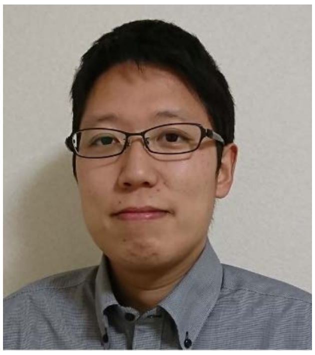


Fig. 1Facile and efficient removal of tungsten anions using lysine-promoted precipitation for recycling high-purity tungsten

References

1. Nakakura, et al., Cationic defect engineering for controlling the infrared absorption of hexagonal cesium tungsten bronze nanoparticles, *Inorganic Chemistry*, (2019) in press.
2. T. Hirano et al., Synthesis of highly crystalline hexagonal cesium tungsten bronze nanoparticles by flame-assisted spray pyrolysis, *Advanced Powder Technology*, 29(10), 2512-2520 (2018).
3. T. Ogi et al., Nanostructuring strategies in functional fine-particle synthesis towards resource and energy saving applications, *Advanced Powder Technology*, 25(1), 3-17 (2014).
4. T. Ogi et al., A simple, rapid, and environmentally friendly method for selectively recovering tantalum by guanidine-assisted precipitation, *ACS Sustainable Chemistry & Engineering*, 6(8), 9585-9590 (2018).
5. T. Ogi et al., Facile and efficient removal of tungsten anions using lysine-promoted precipitation for recycling high-purity tungsten, *ACS Sustainable Chemistry & Engineering*, 5(4), 3141-3147 (2017).

	Nao Tsunoji
	Applied Chemistry, Graduate School of Engineering, Hiroshima University, Assistant Professor
	tnao7373@hiroshima-u.ac.jp
	https://home.hiroshima-u.ac.jp/catalche/index.html

Research keywords: zeolite, layered silicate, mesoporous silica, solid-state NMR, ethanol-to-olefin, NH_3-SCR, photo-catalysis, selective oxidation, epoxidation, KA-oil.

I'm interested in silicon oxide based functional materials such as microporous material zeolite, and its related material layered silicates. I'm trying taller-made synthesis of zeolite via nano-meter order precursor that can prepared by intentional manner. The synthesis strategy using starting zeolite[1,2] and stepwise synthesis gel preparation[3] gave useful physicochemical property of the obtained zeolite that cannot be realized by using general synthesis method.

Frameworks of the layered silicates are similar to the zeolite framework, whereas as the interlayer surfaces are covered with silanol groups, the material are easily functionalized by various modifications. Recently, I reported the successful syntheses and structural analyses of new layered silicates, the Hiroshima University Silicates (HUS-x series).[4-6]

The obtained zeolite material revealed the excellent catalytic stability and activity in bio-ethanol to light olefin, selective catalytic reduction of NOx with ammonia, and basic acid catalysis reaction.[7] In contrast, the layered silicate material modified by various gest unit (such as silane coupling agents, metal complexes) were useful catalysts for selective oxidation of hydrocarbon using oxidant [8,9] and/or under photo-irradiation [10]. I also measured solid-state (MAS) NMR of variety material. I would collaborate by using the NMR skill as well as the synthesis skill of above materials.

Reference. [1] Sonoda, T. *et al. J. Mater. Chem. A* **3**, 857-865, (2015). [2] Takata, T., Tsunoji, N., Takamitsu, Y., Sadakane, M. & Sano, T. *Microporous Mesoporous Mater.* **246**, 89-101, (2017). [3] Joichi, Y. *et al. Cryst. Growth Des.* **18**, 5652-5662, (2018). [4] Tsunoji, N., Ikeda, T., Ide, Y., Sadakane, M. & Sano, T. *J. Mater. Chem.* **22**, 13682-13690, (2012). [5] Tsunoji, N. *et al. J. Mater. Chem. A* **1**, 9680-9688, (2013). [6] Tsunoji, N., Ikeda, T., Sadakane, M. & Sano, T. *J. Mater. Chem. A* **2**, 3372-3380, (2014). [7] Kakiuchi, Y. *et al. Appl. Catal. A-Gen.* **575**, 204-213, (2019). [8] Fukuda, M. *et al. J. Mater. Chem. A* **3**, 15280-15291, (2015). [9] Tsunoji, N. *et al. ChemCatChem* **10**, 2536-2540, (2018). [10] Tsunoji, N. et al. *ACS Catal* DOI:10.1021/acscatal.9b01284.

Ken Sakai
Professor, Department of Chemistry, Faculty of Science, Kyushu University; Principal Investigator, International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University; Professor, Center for Molecular Systems (CMS), Kyushu University
ksakai@chem.kyushu-univ.jp
http://www.scc.kyushu-u.ac.jp/Sakutai/sakai_group_top.html

Kosei Yamauchi
Assistant Professor, Department of Chemistry, Faculty of Science, Kyushu University, International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University
kyamauchi@chem.kyushu-univ.jp
http://www.scc.kyushu-u.ac.jp/Sakutai/sakai_group_top.html

Research keywords: Artificial Photosynthesis, Molecular Catalysis, Water Oxidation, Hydrogen Evolution, CO_2 reduction, Photocatalysis, Homogeneous Electrocatalysis, Kinetics, DFT calculations

Over the past decade, our group has focused on the molecular systems relevant to photosynthetic molecular devices.[1-11] Our targets involve the studies on (i) water oxidation catalysis in order to uptake protons and electrons required for fuels generation, (ii) catalytic water or CO_2 reduction into sustainable fuels (*i.e.*, H_2, CO, etc.), (iii) artificial light-harvesting systems towards the effective charge separation and/or migration, and so on. In order to develop the more desirable/efficient systems in promoting all relevant processes, substantial efforts have been devoted to more carefully study the reaction kinetics and equilibria in solution that are relevant to each topic. Various techniques have been adopted to better understand the mechanistic aspects relevant to all of our systems. Some of the reaction steps of interest are not observable by any experimental techniques, and must be discussed on the basis of our DFT results, which also greatly helped us understand the mechanism of reactions. Importantly, one of our findings is that, in any catalysis, the reactivity of metal(s) can be rationally tuned by use of redox active ligands that are more or less hybridized with metal(s) in their orbitals. Such issues are often involved in our discussion. Our studies have provided new aspects on photo-induced multi-charge separation,[5] near-infrared-driven water reduction,[4] water oxidation catalysis using various transition metal complexes,[1,9,11] non-precious metal based water reduction,[2,6,10] photoelectrochemical cells for the overall water splitting,[3,7] and cobalt porphyrin CO_2 reduction catalysis in fully aqueous media.[8]

As part of these studies, our group reported that a monocobalt polyoxometalate (Co-POM-Mo) and dicobalt (Co_2-POM-Mo) polyoxometalates (Figure 1) serves as an efficient homogeneous water oxidation catalyst (WOC) in the well-known $[Ru(bpy)_3]^{2+}/S_2O_8^{2-}$ photochemical system.[1] Under our experimental conditions, we found that both Co-POM-Mo and Co_2-POM-Mo are capable of catalyzing water oxidation, and exhibit greater turnover frequencies and turnover numbers relative to the previously reported tetracobalt polytungstate Co_4-POM-W ($[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$).

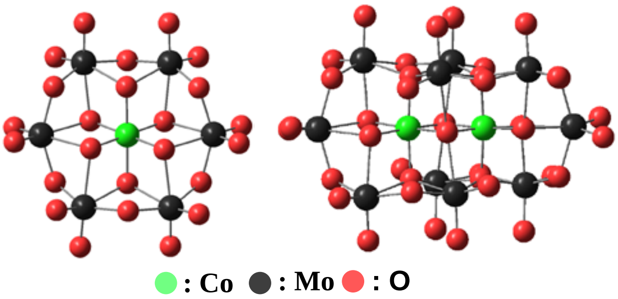


Figure 1. Co-POM-Mo and Co_2-POM-Mo.

Our very recent studies involve attempts to clarify the mechanism of water oxidation by the simplest Co POM catalyst, i.e., Co-POM-Mo.[11] Using $[Ru^{III}(bpy)_3](ClO_4)_3$ as a sacrificial oxidant, a reaction of Co-POM-Mo and $[Ru^{III}(bpy)_3]^{3+}$ has been observed using the stopped-flow technique at various catalyst concentrations and different temperatures to estimate the activation parameters for this reaction. Importantly, our DFT results are in favor of the development of a peroxo-bridged fragment via the O-O bond formation between the Co- and Mo-bound oxygen atoms upon two-electron oxidation.[11]

Possible collaboration: Automatic H_2/O_2 gas measurement, Low temperature stopped-flow, Nanosecond Transient absorption spectroscopy, Picosecond luminescence lifetime measurement, DLS, Homogeneous electrocatalysis (TOF and overpotential estimation), Mechanistic investigation based on DFT calculations, and so on.

References.

[1] S. Tanaka, M. Annaka, K. Sakai, *Chem. Commun.* **2012**, *48*, 1653.

[2] K. Koshiba, K. Yamauchi, K. Sakai, *Angew. Chem. Int. Ed.* **2017**, *56*, 4247.

[3] K. Takijiri, K. Morita, T. Nakazono, K. Sakai, H. Ozawa, *Chem. Commun.* **2017**, *53*, 3042.

[4] Y. Tsuji, K. Yamamoto, K. Yamauchi, K. Sakai, *Angew. Chem. Int. Ed.* **2018**, *57*, 208 (***Inside Cover***).

[5] K. Yamamoto, A. Call, K. Sakai, *Chem. Eur. J.* **2018**, *24*, 16620 (***VIP***).

[6] Y. Aimoto, K. Koshiba, K. Yamauchi, K. Sakai, *Chem. Commun.* **2018**, *54*, 12820.

[7] K. Morita, K. Sakai, H. Ozawa, *ACS Appl. Energy Mater.* **2019**, *2*, 987.

[8] A. Call, M. Cibian, K. Yamamoto, T. Nakazono, K. Yamauchi, K. Sakai, *ACS Catal.* **2019**, *9*, 4867.

[9] A. R. Parent, T. Nakazono, Y. Tsubonouchi, N. Taira, K. Sakai, *Adv. Inorg. Chem.*, **2019**, *74*.

[10] J.-W. Wang, K. Yamauchi, H.-H. Huang, J.-K. Sun, Z.-M. Luo, D.-C. Zhong, T.-B. Lu, K. Sakai, *Angew. Chem. Int. Ed.*, **2019**, DOI: 10.1002/anie.201904578.

[11] N. Taira, K. Yamauchi, K. Sakai, *Submitted*.

<table>
<tr><td rowspan="4"></td><td>Osamu Ishitani</td></tr>
<tr><td>Tokyo Institute of Technology, Professor</td></tr>
<tr><td>ishitani@chem.titech.ac.jp</td></tr>
<tr><td>http://www.chemistry.titech.ac.jp/~ishitani/en/index_en.html</td></tr>
</table>

Research keywords: Ring-shaped Re(I) complexes, CO_2 Reduction, Photosensitizer, Multi-electron accumulation

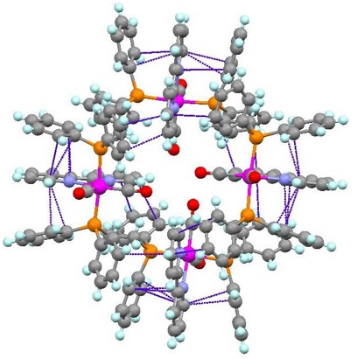


Fig. 1. Ring-shaped Re(I) tetranuclear complex.

We have successfully synthesized a novel type of ring-shaped rhenium(I) polymers bridged with bidentate phosphorus ligands (Re-ring) by using photochemical ligand substitution reactions which we have reported previously. These Re-rings can emit at room temperature even in solution, and the emission quantum yields are much higher than those of the corresponding Re(I) mononuclear complexes. The structure of Re-ring with dppe (PPh_2-CH_2-CH_2-PPh_2) as bridge ligands was determined by X-ray crystallographic analysis as shown in Fig. 1. It has a ship-flapped structure, and intramolecular interactions were observed between the bipyridine ligands and the phenyl groups on the bidentate phosphorus ligands. Some Re-rings can work as redox photosensitizers in photocatalytic CO_2 reduction. For example, The combination of a trinuclear Re-ring photosensitizer with fac-$[Re(bpy)(CO)_3(MeCN)]^+$ (bpy = 2,2'-bipyridine) as a catalyst photocatalyzed CO_2 reduction with the highest quantum yield of 82%.

Reference.

1. Morimoto, T.; Nishiura, C.; Tanaka, M.; Rohacova, J.; Nakagawa, Y.; Funada, Y.; Koike, K.; Yamamoto, Y.; Shishido, S.; Kojima, T.; Saeki, T.; Ozeki, T.; Ishitani, O., *J. Am. Chem. Soc.* **2013,** *135*, 13266.
2. Yamazaki, Y.; Rohacova, J.; Ohtsu, H.; Kawano, M.; Ishitani, O., *Inorg. Chem.* **2018,** *57*, 15158.
3. Rohacova, J.; Ishitani, O., *Chem. Sci.* **2016,** *7*, 6728.
4. Rohacova, J.; Sekine, A.; Kawano, T.; Tamari, S.; Ishitani, O., *Inorg. Chem.* **2015,** *54*, 8769.
5. Asatani, T.; Nakagawa, Y.; Funada, Y.; Sawa, S.; Takeda, H.; Morimoto, T.; Koike, K.; Ishitani, O., *Inorg. Chem.* **2014,** *53*, 7170.

Masato Hashimoto

Professor
Department of Systems Engineering, Faculty of Systems Engineering, Wakayama University

mh1043@wakayama-u.ac.jp

http://web.wakayama-u.ac.jp/~mh1043/index.html

Research keywords: peroxopolyoxometalates, structure, synthesis, formation reaction, NMR

Our research is focused on the basic chemistry of peroxopolyoxometalates. Our main targets at present are:

1. Peroxovanadates with various heteroatom group(s) such as orthophosphate and linear/circular polyphosphates. Some novel peroxopolyphosphatovanadates were isolated and structurally analyzed. NMR (^{31}P and ^{51}V) investigation on their aqueous behavior is going on.
2. Peroxoisomolybdates and -tungstates with rare earth atoms. A series of novel type peroxomolybdates and -tungstates with two rare earth (III) atoms were isolated and structurally analyzed. Elucidation of their formation by NMR (^{95}Mo, ^{183}W, ^{89}Y and ^{139}La), and measurements of their physical properties are in progress.
3. Peroxoheteropolymolybdates and -tungstates having linear and circular polyphosphate(s). Several polyanions with diphosphate(s) were obtained and their structures were determined. The complex formation in the aqueous molybdate/tungstate - diphosphate - hydrogen peroxide systems is quite complicated, and the investigation is going on mainly by ^{31}P NMR.
4. Peroxoheteropolymolybdates and -tungstates with (mono)phosphate(s), sulfate(s) or borate(s) as heteroatom group(s). Various anions have been isolated and structurally analyzed. The aqueous reaction systems are also complicated, and elucidation of complex formation in each system is attempted by NMR (^{31}P, ^{11}B, ^{95}Mo, ^{183}W and ^{17}O).

Synthetic and structural studies on peroxoisopolumolybdates/tungstates, and peroxoheteropolymolybdates/tungstates with rare earth (III), are also attempted. In the peroxopolyoxometalate reaction systems the (addenda atom)/(hydrogen peroxide) molar ratio is essential in addition to usual conditions important for the formation of polyoxometalates. However, as the peroxide is not stable in the reaction system (and changes of other conditions such as pH followed by the decomposition of the peroxide) it is difficult to keep all the reaction conditions under control. We often have a problem to get good reproducibility due to this reason, and thus no detailed result is given here.

<table>
<tr><td rowspan="4"></td><td>Ryo Tsunashima</td></tr>
<tr><td>Associate Professor, Yamaguchi University</td></tr>
<tr><td>ryotsuna@yamaguchi-u.ac.jp</td></tr>
<tr><td>http://web.cc.yamaguchi-u.ac.jp/~ryotsuna/tsunashima/index.html
https://publons.com/researcher/1445682/ryo-tsunashima/</td></tr>
</table>

Research keywords: electrical conduction, dielectric property, chromism, hydrogen bond,

Molecular solid and molecule for materials science

Solids state properties of the molecular solids are main focus of the research project. Dynamic behaviors of varieties of molecule (polyoxometalate, organic, inorganic, coordination compound) and electrons under the electric field are interested, that includes

- Electrical conduction; organic semiconductor, charge transfer complex
- Ionic conduction; electrophoretic migration, solid-state electrolyte
- Dielectric property; ferroelectrics, pyroelectrics, dipole relaxation, charge polarization.

In addition, controlling and understanding of sophisticated intermolecular interaction system is another interest that includes,

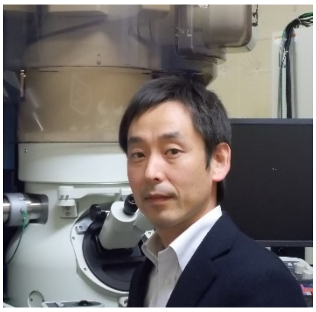
- Rational synthesis of polyoxometalates,
- Molecular assembly nanostructure,
- Chromism; charge transfer, redox,

A work and interests about POMs are summarized in review paper.[1] Corroboration project is welcome to measure dielectric constant, electric conductivity, temperature variable FT-IR/UV-VIS-NIR spectra, microscope FT-IR.

Reference. Researcher ID: D-2800-2011

[1] Y. F. Song and R. Tsunashima “Recent advances on polyoxometalates-based molecular and composite materials”***Chem. Soc. Rev***., *41*, 7384-7402 (2012).

[2] D.-L. Long, R. Tsunashima, L. Cronin "Polyoxometalates: Building Blocks for Functional Nanoscale Systems", ***Angew. Chem. Int. Ed.***, *49*, 1736-1758 (2010)



Norihito Hiyoshi

Senior Researcher, Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST)

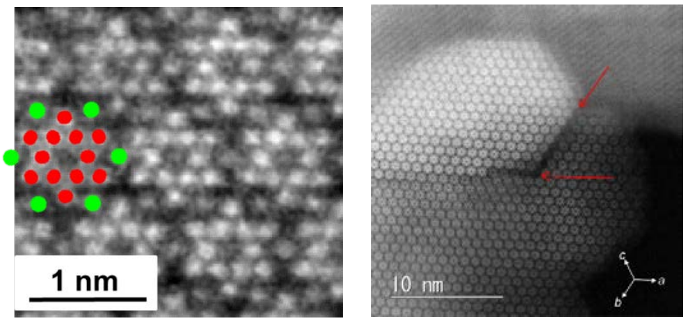
n-hiyoshi@aist.go.jp

Research keywords: Scanning transmission electron microscopy, Catalyst characterization.

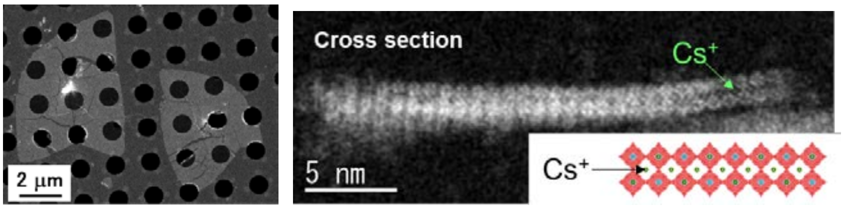
One of my research interests is high-resolution imaging of catalytic materials by (scanning) transmission electron microscopy ((S)TEM). (S)TEM is effective in investigating molecular arrangement of polyoxometalates, though polyoxometalates are electron beam-sensitive and difficult to observe. Defect structures of Keggin-type polyoxometalate crystallites were elucidated by direct observation using STEM [1].

I am also interested in the development of catalytic materials. Keggin-type polyoxometalate nanosheets were synthesized and their structures were determined by STEM [2].

In addition, I have been collaborating with some research groups in the (S)TEM observation of catalytic materials including polyoxometalates, zeolites, supported metal catalysts, and various nanomaterials.



STEM images of $Cs_xH_{4-x}SiW_{12}O_{40}$ [1]



STEM images of Keggin-type polyoxometalate nanosheets [2]

[1] N. Hiyoshi and Y. Kamiya, *Chem. Commun.*, 2015, **51**, 9975-9978.

[2] N. Hiyoshi, *Chem. Commun.*, 2018, **54**, 5217-5220.

Nobuhiro Yasuda

Research Scientist
Japan Synchrotron Radiation Research Institute (JASRI)

nyasuda@spring8.or.jp

http://rud.spring8.or.jp/member/0004977.html

Research keywords: Synchrotron radiation, SPring-8, Single crystal structure analysis, X-ray diffraction, Small crystal

The research field is the chemical crystallography. In particular, the chemical reactions in single crystal are my research interest. For realizing my target research, the structure analysis of sub-micrometer size small crystals [1, 2] and the sub-millisecond rapid measurement [3] have been developing using the synchrotron radiation of SPring-8.

The public beamlines in SPring-8, BL02B1 and BL40XU, are available for the single crystal structure analysis of small molecules. I support the beamline users for achievement of their experiments as a beamline scientist at both beamlines.

In the former collaboration, I have carried out the structure analyses of micro- and sub-micrometer sized polyoxometalate and other metal oxide crystals [4-7]. The crystal structure analysis of before and after reaction are useful for not only determination of the chemical structure but also elucidation of the mechanism of catalysis. I will collaborate with the members who want to analyze the crystal/molecular structure of the single crystals which are difficult to measure in the laboratory system. Furthermore, the structure analysis and the other experiments using the synchrotron radiation (powder XRD, X-ray spectroscopy and so on) will be supported.

References.

[1] N. Yasuda *et al.*, *J. Synchrotron Radiat.*, **16**, 352-357 (2009).

[2] N. Yasuda *et al.*, *AIP Conf. Proc.*, **1234**, 147-150 (2010).

[3] N. Yasuda *et al.*, *AIP Conf. Proc.*, **2054**, 050007 (2019).

[4] Z. Zhang *et al.*, *Inorg. Chem.*, **53**, 903-911 (2014).

[5] S. Ogo *et al.*, *Inorg. Chem.*, **53**, 3526-3539 (2014).

[6] Z. Zhang *et al.*, *Nat. Commun.*, **6**, 7731 (2015).

[7] S. Ishikawa *et al.*, *J. Phys. Chem. C*, **119**, 7195-7206 (2015).

	Takeshi Nitta
	Nippon Inorganic Colour & Chemical Co.,Ltd. Research manager Technical div.
	nitta@muki.co.jp
	http://www.muki.co.jp/english/index.html

Nippon Inorganic Colour & Chemical Co.,Ltd. is manufacturer specializing in the manufacture and sales of industrial chemicals with focus on high-value-added products such as molybdenum and tungsten compounds and heteropoly acid, which are expected in further market expansion following the development of the petroleum refining and petroleum industry.

Molybdenum Manufactured Product Lines

- Ammonium Molybdate
- Sodium molybdate
- Molybdenum trioxide
- Molybdic acid

Tungsten Manufactured Product Lines

- Ammonium paratungstate
- Ammonium metatungstate (crystal & aqueous solution type)
- Sodium tungstate
- Tungsten trioxide
- Tungstic acid

Heteropoly acid Manufactured Product Lines

Crystal type & Aqueous Solution type(HPAs contains approximately 40~50 wt%)

- Phosphomolybdic acid
- Phosphotungstic acid
- Silicotungstic acid

Special Products

- Silicomolybdic acid
- Phosphotungstic acid Type-7 (crystal water is approximately 7)
- Complex Type (e.g. Phosphovanadomolybdic acid)