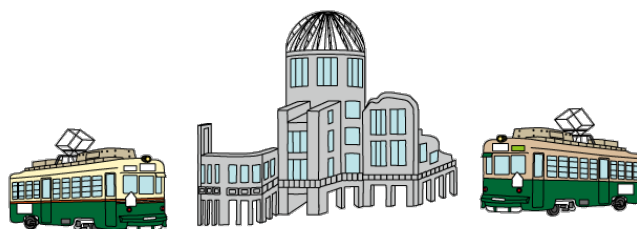


Abstracts

Pre-Xmas Meeting 2023

of

EPSRC-JSPS Core-to-Core Collaboration Program
International Network on Polyoxometalate Science
for Advanced Energy Materials (INPOMs)



Date: 13th and 14th December, 2023

International Conference Center Hiroshima, Hiroshima, Japan

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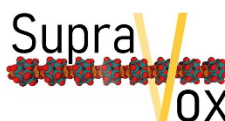
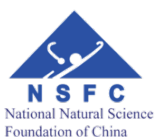


研究拠点形成事業
Core-to-Core Program



EPSRC


Engineering and Physical Sciences
Research Council



Abstract Number, Participants, and Affiliation

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Research keywords: Rechargeable Batteries, Polyoxometalates, Nanocarbons

Battery Performances of Polyoxometalates/Nanocarbon Nanohybrid Materials

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, in which the cathode active materials are polynuclear metal complexes. We have used a Keggin-type polyoxometalate (POM) cluster, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, 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, but the cycle performance is still poor probably due to structural decomposition. Furthermore, we performed nanohybridization between POM and nanocarbons, wherein all POM cluster molecules were independently bonded to nanocarbons, such as single-walled carbon nanotubes and conductive agents, such as reduced graphene oxides. Nanohybridization induces effective electron transfer to POM via nanocarbons, effectively diffuse and retain Li^+ ions from the electrolyte, and improves capacitance owing to the electrical double layer capacitance (EDLC) of nanocarbons, leading to a higher capacity and an improved charge/discharge rate. Nanocarbons with higher surface areas have correspondingly higher EDLCs, which improve the pseudo-capacitance of these nanohybrid materials. This indicates that the use of nanocarbons with an even larger surface area may result in higher capacities when subjected to high current densities. Therefore, hybridization with nanocarbons increases their original EDLCs.

Herein, we selected carbon nanohorns (CNHs) as the nanocarbon material, as they exhibit good electrical conductivity, stable mechanical strength, large surface areas, and more active sites, to explore the performance of POM hybrid materials. As a result, the POM/CNH hybrid materials maintain a high battery capacity even at high current densities in charge/discharge tests, and the observed capacity was higher than other POM/nanocarbon hybrid materials.

Reference.

[1] Hirofumi Yoshikawa et al., *Batteries&Supercaps* (2023), 6, e202200385

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Research keywords: molecular oxide, molybdoplatinate, hydrogen-bonded oligomers, solution

Mutual Transformation of Hydrogen-Bonded Molybdoplatinate Oligomers in Solution

A while back, Klemperer et al. reported the synthesis and solid state structures of the hydrogen-bonded hexamolybdoplatinate tetramer and trimer, $[\text{H}_{23}(\text{PtMo}_6\text{O}_{24})_4]^{9-}$ and $[\text{H}_{16}(\text{PtMo}_6\text{O}_{24})_3]^{8-}$ [1]. A few years later, we reported the formation and the crystal structure of the hydrogen-bonded tetramer of hexatantalate, $[\text{H}_{18}(\text{Ta}_6\text{O}_{19})_4]^{14-}$ [2]. We also found that this tetramer stayed intact in solution. Do the molybdoplatinate oligomers also exist in solution without falling apart? Is it possible to transform them into each other in solution? We investigated the solution behavior of the oligomers to address these questions.

A series of NMR experiments confirmed that both the trimer and tetramer stay intact in solution as well as the dimer, $[\text{H}_9(\text{PtMo}_6\text{O}_{24})_2]^{7-}$ [3] (Figure 1). The NMR spectra also revealed that the tetramer disassembles to form the trimer and then the dimer by the action of a base and the dimer assembles into the trimer and tetramer by the action of an acid.

References.

[1] Day, V. W.; Goloboy, J. C.; Klemperer, W. G., *Eur. J. Inorg. Chem.*, **2009**, 5079-5087.

[2] Matsumoto, M.; Ozawa, Y.; Yagasaki, A., *Inorg. Chem.* **2021**, 51, 5991-5993.

[3] Ikegami, S.; Kani, K.; Ozeki, T.; Yagasaki, A., *Chem. Commun.*, **2010**, 46, 785-787.

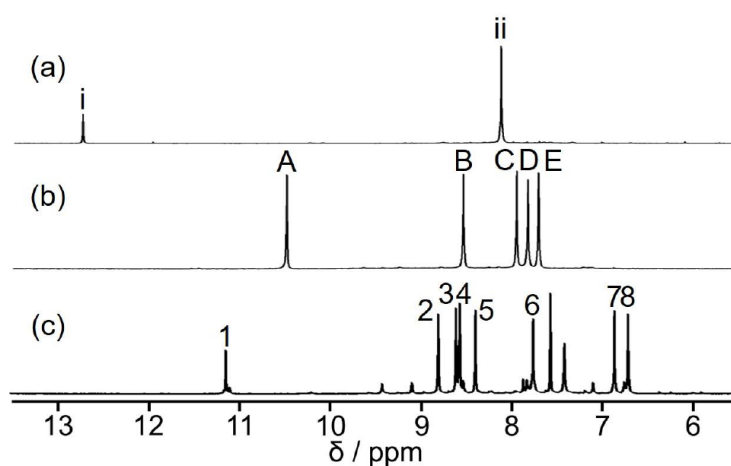



Figure 1. ^1H NMR spectra of $\text{TBA}_7[\text{H}_9(\text{PtMo}_6\text{O}_{24})_2]$ (a), $\text{TBA}_8[\text{H}_{16}(\text{PtMo}_6\text{O}_{24})_3]$ (b), and $\text{TBA}_9[\text{H}_{23}(\text{PtMo}_6\text{O}_{24})_4]$ (c) in CD_3CN (TBA = tetra-*n*-butylammonium).

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Research keywords: Water Oxidation Catalysis, Single-site cobalt water oxidation catalysts, intracluster O-O bond formation, Artificial Photosynthesis, Water Splitting

Single-site Cobalt Water Oxidation Catalysts

Our intense studies on water oxidation catalysis initiated in 2007, resulting in various important achievements demonstrating single-site water oxidation catalysis by Ru-, Fe-, Co-, and Cu-based molecular catalysts.^{1,2} Stimulated by the report on the water oxidation catalysis by cobalt oxide,³ we also paid attention to cobalt-based molecular WOCs. Although some researchers already reported on tetranuclear cobalt polyoxometalates for water oxidation, the first single-site cobalt polyoxomolybdate WOC, together with the first dicobalt one, was evidenced.⁴ As illustrated in Figure 1, the O-O coupling in the single-site cobalt polyoxomolybdate WOC has recently been shown to proceed among the preinstalled oxygen atoms in the cluster via intramolecular O-O coupling.⁵ In addition, the first important examples of cobalt porphyrin WOCs were further evidenced by our group.⁶ More details are also described in our review articles.^{7,8}

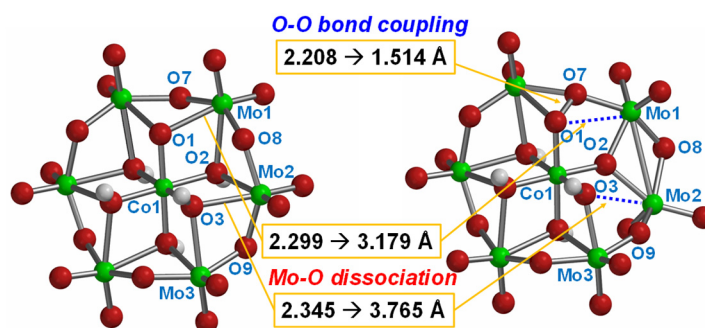



Figure 1. Clarifying the dissociative activation leading to the intracluster O-O coupling by cobalt polyoxomolybdate WOC.

Reference.

1. S. Masaoka, and **K. Sakai**,* *Chem. Lett.* **2009**, *38*, 182-183.
2. A. Kimoto, S. Masaoka, **K. Sakai*** *et al.* *Chem. Commun.* **2012**, *48*, 239-241.
3. M. W. Kanan, and D. G. Nocera, *Science* **2008**, *321*, 1072-1075.
4. S. Tanaka, M. Annaka, and **K. Sakai**,* *Chem. Commun.* **2012**, *48*, 1653-1655.
5. N. Taira, K. Yamauchi, and **K. Sakai**,* *ACS Catal.* **2023**, *13*, 3211-3223.
6. T. Nakazono, A. R. Parent, and **K. Sakai**,* *Chem. Commun.* **2013**, *49*, 6325-6327.
7. A. R. Parent, and **K. Sakai**,* *ChemSusChem* **2014**, *7*, 2070-2080.
8. A. R. Parent, T. Nakazono, Y. Tsubonouchi, N. Taira, and **K. Sakai**,* *Adv. Inorg. Chem.*, **2019**, *74*, 197-240.

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Research keywords: Polyoxometalate, Electrochemistry, simulation, redox mechanism

Electrochemistry of Polyoxometalates

Polyoxometalates (POMs) have excellent electrochemical properties, such as multielectron transfer without the change in their structure and proton and lithium-ion coupling depending on their reduced levels. Electrochemical behavior of POMs has been extensively investigated for a long time. However, there are still unclear aspects since it is very complicated. Our group has investigated on the detailed voltammetric behavior of POMs to elucidate redox mechanism based on simulation of cyclic and large amplitude Fourier transformed alternating current (FTAC) voltammograms with a help of NMR and ESR. We have obtained the excellent results on electrochemistry of POMs during INPOMs projects as follows: 1) Voltammetric behavior of $[V_{in}M_{12}O_{40}]^{3-}$ and $[V_{in}V_{out}M_{11}O_{40}]^{4-}$ ($M=Mo, W$) in CH_3CN [1]; 2) Electron transfer kinetics in framework parts and central part of $[SV_{out}W_{11}O_{40}]^{3-}$, $[V_{in}W_{12}O_{40}]^{3-}$ and $[V_{in}V_{out}W_{11}O_{40}]^{4-}$ in CH_3CN ; 3) Redox mechanism with desorptive process in voltammetric behavior of $[SCuW_{11}O_{39}]^{4-}$ in CH_3CN ; 4) Voltammetric behavior of POMs in ionic liquids and its application to the estimation of A_{NS} and E_T^N s of ionic liquids [2,3]; 5) Voltammetric behavior of POMs-doped poly(3,4-ethylenedioxythiophene) [4]; 6) Development of electrochemical evaluation for antioxidant capacity of beverage by using POMs as redox probes [5]. In this symposium, I will talk on voltammetric behavior of $[V_{in}M_{12}O_{40}]^{3-}$ and $[V_{in}V_{out}M_{11}O_{40}]^{4-}$ ($M=Mo, W$) as well as $[SV_{out}W_{11}O_{40}]^{3-}$ in CH_3CN .

In the case of well-known Keggin type POMs $[XM_{12}O_{40}]^{n-}$ ($X=P, Si; M=Mo, W$), tungsten and molybdenum in the framework are reduced, while central vanadium can be reduced for $[V_{in}W_{12}O_{40}]^{3-}$ and $[V_{in}V_{out}W_{11}O_{40}]^{4-}$. Elucidation of similarity and difference in electron transfer to framework and central atoms should be of great significance to understand voltammetric behavior of POMs. FTAC voltammetry has been used to determine heterogeneous electron transfer kinetics in framework parts and a central part of $[SV_{out}W_{11}O_{40}]^{3-}$, $[V_{in}W_{12}O_{40}]^{3-}$ and $[V_{in}V_{out}W_{11}O_{40}]^{4-}$ in CH_3CN

References: [1] S. Yokoyama, S. Azuma, Y. Eguchi, K. Kodani, T. Hasegawa, S. Ogo, H. Ota, S. Guo, J. Boas, J. Zhang, A. Bond, T. Ueda, *Inorg. Chem.*, in press.; [2] H. Ishida, S. Azuma, N. Yamasaki, H. Kurita, T. Hasegawa, S. Ogo and T. Ueda, *Anal. Sci.*, **2021**, 37, 1131-1137.; [3] J. I. Phillips, S. Azuma, J. Lee, T. Ueda and D. S. Silvester, *Aust. J. Chem.*, **2022**, 75, 865-876.; [4] I. Sakthnathan, N. Yamasaki, D. Barreca, C. Maccato, T. Ueda and T. McCormac, *Electrochim. Acta*, **2023**, 462.; [5] H. Ishida, N. Yamasaki, Y. Otsuka, D. Mori, T. Shimamura, T. Hasegawa, S. Ogo and T. Ueda, *Anal. Sci.*, **2022**, 38, 151-156.; [6] T. Ueda, *Anal. Sci.*, **2021**, 37, 107-118.

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Research keywords: Catalyst, Hydrogen Peroxide, Oxidation, Peroxotungstate

Oxidation of Alkenes with Hydrogen Peroxide Catalyzed by Sodium Salt of $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{9-}$ (Ln = lanthanide)

Aqueous hydrogen peroxide serves as an exemplary clean oxidant, garnering significant interest in transition-metal catalysts for the oxidation of organic compounds. The interaction of H_2O_2 with polyoxometalate forms peroxy ligands at the metal site is crucial for the oxidation of organic compounds. We previously reported the cyclooctene epoxidation process using H_2O_2 , catalyzed by vanadium-substituted Lindqvist-type polyoxotungstate, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[\text{VW}_5\text{O}_{19}]$. ESI-MS spectra demonstrated multiple peroxidations at both V and W sites, with the V(peroxy) site acting as the critical catalytic site, enhanced synergistically by the W(peroxy) site.^[1] This study presents alkene oxidation using 30% H_2O_2 and sodium salts of polyoxotungstolanthanoate, $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{9-}$ (Ln = lanthanide), which exhibited substantial catalytic activity in *phase transfer reagent-free* conditions, both *with* and *without organic solvents*. Specifically, $\text{Na}_9[\text{Eu}(\text{W}_5\text{O}_{18})_2] \cdot 32\text{H}_2\text{O}$ facilitated cyclooctene epoxidation in an acetonitrile/cyclooctene/ H_2O_2 system, achieving 95% conversion and 98% selectivity for cyclooctene oxide. Moreover, $\text{Na}_9[\text{Eu}(\text{W}_5\text{O}_{18})_2] \cdot 32\text{H}_2\text{O}$ efficiently catalyzed cyclohexene oxidation to adipic acid under solvent-free conditions, yielding a 97% conversion rate and 89% selectivity. The conversion to adipic acid involved multiple oxidative reactions (cyclohexene epoxidation, alcohol oxidation, Baeyer–Villiger oxidation) and hydrolyzes.^[2] In our experiments, we successfully isolated two peroxotungstates, $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ ^[3] and $[\text{W}_6\text{O}_6(\text{O}_2)_{10}(\text{H}_2\text{O})_6]^{2-}$, from oxidation system catalyzed by $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{3-}$ (Figure 1). Crystal structure and HPLC analyses revealed the complete decomposition of the $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{3-}$ anion to $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ and $[\text{W}_6\text{O}_6(\text{O}_2)_{10}(\text{H}_2\text{O})_6]^{2-}$ by H_2O_2 in this system. The O atom is directly transferred from the peroxy ligand of peroxotungstates to the alkene. By adding only $\text{Na}_9[\text{Eu}(\text{W}_5\text{O}_{18})_2] \cdot 32\text{H}_2\text{O}$, a simple and effective catalytic oxidation system was established, eliminating the need for pH adjustments or the addition of various ions. Therefore, $\text{Na}_9[\text{Eu}(\text{W}_5\text{O}_{18})_2] \cdot 32\text{H}_2\text{O}$ serves as an exemplary precursor of oxidation catalysts.

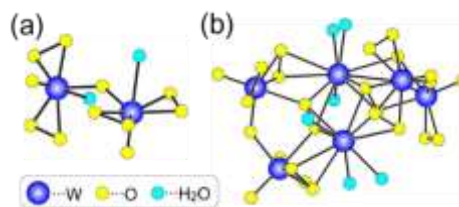



Figure 1. Structure of $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ (a) and $[\text{W}_6\text{O}_6(\text{O}_2)_{10}(\text{H}_2\text{O})_6]^{2-}$ (b).

Reference.

- [1] E. Ishikawa, D. Kihara, Y. Togawa, C. Ookawa, *Eur. J. Inorg. Chem.*, **2019**, 402-409
- [2] K. Sato, M. Aoki, R. Noyori, *Science*, **1998**, 281, 1646-1647.
- [3] (a) K. Kamata, K. Yamaguchi, S. Hikichi, N. Mizuno, *Adv. Synth. Catal.* **2003**, 345, 1193-1196; (b) K. Kamata, K. Yamaguchi, N. Mizuno, *Chem, Eur. J.* **2004**, 10, 4728-4734.

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Research keywords: Polyoxometalate, Silver ethynide, Organic—inorganic hybrid cluster

Polyoxometalate—silver ethynide mixed clusters

Silver clusters show a diverse range of structures depending on their protecting ligands and templating anions. Among various protecting ligands, the *tert*-butylethynide ligand is widely used. A typical synthetic approach of such *tert*-butylethynide-protected silver clusters is first to dissolve insoluble silver *tert*-butylethynide, $\text{AgC}\equiv\text{C}(\text{CH}_3)_3$, by mixing with certain silver salts such as trifluoromethanesulfonate or hexafluorophosphate. The addition of chelating ligands, such as tetramethyl ethylenediamine, facilitates the dissolution.

In such intermediate solutions, silver atoms should exist in some soluble forms, presumably as smaller clusters. We are interested in the identification and isolation of such smaller clusters because (i) it would give information on the solution structure of the silver clusters and (ii) isolated smaller clusters could be used as stoichiometrically well-defined starting materials for synthesizing larger clusters.

By lowering the solution temperature down to $-20\text{ }^\circ\text{C}$, we succeeded in crystallizing $[\text{Ag}_3\{\text{C}\equiv\text{CC}(\text{CH}_3)_3\}\{(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\}_3]^{2+}$ (Fig. 1 left) and $[\text{Ag}_8\{\text{C}\equiv\text{CC}(\text{CH}_3)_3\}_4\{(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\}_4]^{4+}$ (Fig. 1 right) as PF_6^- and CF_3SO_3^- salts, respectively.

By using these clusters as precursors, we have obtained novel polyoxometalate—silver ethynide mixed clusters, examples of which are $[\text{Ag}_{42}(\text{CO}_3)\{\text{C}\equiv\text{CC}(\text{CH}_3)_3\}_{27}(\text{CH}_3\text{CN})_2(\beta\text{-H}_2\text{W}_{12}\text{O}_{40})_2]^{+}$ and $[\text{Ag}_4\{\text{C}\equiv\text{CC}(\text{CH}_3)_3\}\{(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\}_2(\text{Mo}_8\text{O}_{26})^-]_{\infty}$.

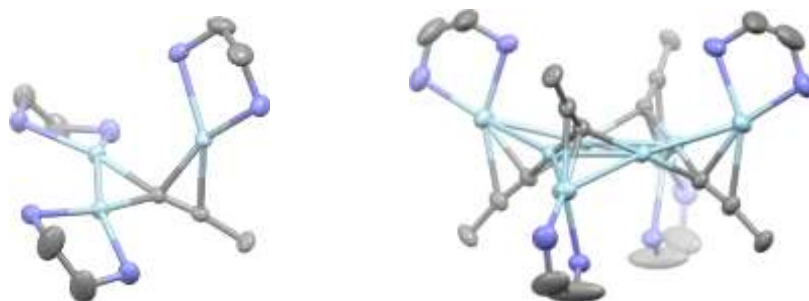


Figure 1. Discrete smaller silver clusters used as precursors of polyoxometalate—silver ethynide mixed clusters: $[\text{Ag}_3\{\text{C}\equiv\text{CC}(\text{CH}_3)_3\}\{(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\}_3]^{2+}$ (left) and $[\text{Ag}_8\{\text{C}\equiv\text{CC}(\text{CH}_3)_3\}_4\{(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\}_4]^{4+}$ (right). Methyl groups and hydrogen atoms are not shown for clarity.

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Research keywords: Polyoxovanadates, Fluoride, Epoxidation, Peroxide

Synthesis and Catalysis of Polyoxovanadate

Oxidation catalysis of vanadium compounds is the attractive perspective not only in biocatalysts and homogeneous molecular catalysts but also in practical solid catalysts. Among them, peroxo-vanadium complexes are the key active species. In most cases of solid catalysts, it is difficult to investigate the actual active species on the surface of solid catalysts. Elucidation of structures of active vanadium species on inorganic materials and of their reaction mechanisms helps the deeper comprehension of vanadium catalysts.

Due to the strong template effect of fluoride to anionic vanadium clusters, fluoride-incorporated polyoxovanadate derivatives were prepared.^[1] By acidification of previously reported $[\text{HV}_{11}\text{O}_{29}\text{F}_2]^{4-}$ (V11), catalytic performance was improved at the same time as structure transformation to $[\text{V}_{12}\text{O}_{30}(\text{O}^t\text{Bu})\text{F}_2]^{3-}$ (V12-O^tBu). Compound V12-O^tBu possess tetrahedrally coordinated vanadium unit on V11. By the reaction of V12-O^tBu and ^tBuOOH, $[\text{V}_{12}\text{O}_{30}(\text{OO}^t\text{Bu})\text{F}_2]^{3-}$ (V12-OO^tBu) was obtained by the ligand exchange to the peroxo in a side-on fashion, which is similar structure to that of the peroxo form of vanadium haloperoxidase. Via the catalytic cycle between V12-O^tBu and V12-OO^tBu, epoxidation and bromination of alkene proceeded (Figure).^[2]

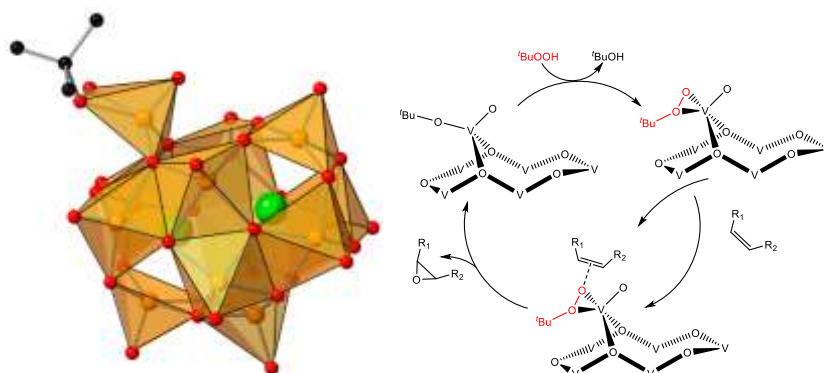


Figure Structures of V12-OO^tBu and proposal reaction mechanism of V12-O^tBu via V12-OO^tBu for epoxidation of alkene.

Reference.

[1] Y. Kikukawa, T. Yokoyama, S. Kashio, Y. Hayashi, *J. Inorg. Biochem.* 147 (2015) 221.

[2] Y. Kikukawa, Y. Sakamoto, H. Hirasawa, Y. Kurimoto, H. Iwai, Y. Hayashi, *Catal. Sci. Technol.* 12 (2022) 2438.



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Research keywords: Solid catalyst, Low-temperature catalytic system, Electric field

Preparation of polyoxometalate-derived complex metal oxide supported catalysts for low-temperature redox reaction

We have developed unconventional reaction system, a catalytic reaction under an electric field, to proceed various chemical reactions at low temperatures [1]. Notably, metal oxide catalysts prepared from polyoxometalate exhibited the high activity for several redox reactions under the electric field at low temperatures [1,2]. Herein, we report preparations of Ce-W-O and Pt/MoO_x/ZrO₂ system catalysts and their catalytic activity for oxidative coupling of methane (OCM) and CO₂ hydrogenation under the electric field at low temperatures.


Oxidative coupling of methane (OCM) over Ce-W-O system catalysts: Direct catalytic methane conversion to C₂ hydrocarbons by OCM is an attractive catalytic process, however, activation of methane requires high temperatures over 973 K even though using well-established multi-component oxide catalysts and non-selective oxidation proceeds at such high temperatures. To solve this problem, we developed new metal oxide catalysts and adopted the low temperature reaction system under the electric field. Ce₂(WO₄)₃/CeO₂ catalyst was prepared from the reaction between tetrabutylammonium salt of Keggin-type PW₁₂O₄₀³⁻ and CeO₂. This Ce-W-O system catalysts showed high OCM activity under the electric field even at 423 K while the catalyst showed low OCM activity in thermal reactions even at high temperature of 1073 K [2].

CO₂ hydrogenation over Pt/MoO_x/ZrO₂ system catalysts: CO₂ hydrogenation to CO *via* reverse water gas shift (RWGS) is one of promising candidates for CO₂ utilization technologies. Due to the endothermic reaction, RWGS reaction required high temperatures. Therefore, we adopted the low temperature catalytic system with polyoxometalate-derived catalysts for the RWGS reaction. Pt/MoO_x/ZrO₂ catalyst was prepared by a successive impregnation method using a Pt(NH₃)₄(NO₃)₂, an ammonium salt of Anderson-type heptamolybdate and ZrO₂. The prepared catalysts showed the high activity under the electric field even at low temperature of 423 K.

Reference.

[1] S. Ogo, Y. Sekine, *Chem. Rec.*, 17 (2017) 726.

[2] K. Sugiura, S. Ogo, K. Iwasaki, T. Yabe, Y. Sekine, *Sci. Rep.*, 6 (2016) 25154.

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Research keywords: Thermal transformation, Metal oxide, Porous material


Thermal Transformation of Ammonium Oxometalate to Metal Oxide in Porous Materials

It has been well-known that heating the ammonium salt of oxometalates resulted in metal oxides through the release of volatile NH_3 with generating H^+ from NH_4^+ , e.g. $(\text{NH}_4)_2\text{MoO}_4 \rightarrow \text{MoO}_3 + 2\text{NH}_3 + \text{H}_2\text{O}$. Such processes undergo the formations of several types of polyoxometalates as intermediate species, which is similar to the reaction in the solution state. Recently, Sadakane *et al.* reported the thermal transformation of methylammonium monomolybdate to molybdenum(VI) oxide via several steps of the formation of polyoxomolybdates in the crystalline solid-state.¹ Inspired by their related works,²⁻³ our concern was directed to the reactivity and the product of the thermal transformation in a confined space. Namely, our question is what if the reaction occurs in a porous space.

Now we are conducting the thermal transformations of ammonium salts of oxometalates, $(\text{NH}_4)_2\text{MO}_4$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $(\text{NH}_4)\text{VO}_3$ in ZIF-8 which is a famous MOF (Metal Organic Framework). Very recently, we successfully obtained vanadium oxide species supported on ZIF-8 by heating $(\text{MeNH}_3)\text{VO}_3@ZIF-8$. Now their characterizations are in progress with using XRF and IR spectroscopy, gas adsorption, and XPS. Our project has just started. All suggestions are welcome.

Reference.

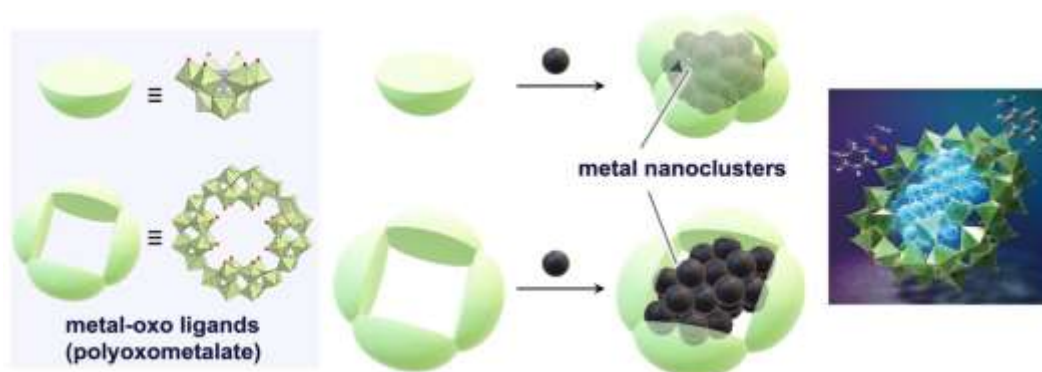
- [1] N. C. Sukmana, Sugiarto, J. Shinogi, T. Kojima, A. Higashiura, A. Yamamoto, T. Sakaguchi, M. Sadakane, *ChemLett*, 2023, **52**, 167-171.
- [2] N. C. Sukmana, Sugiarto, Z. Zhang, M. Sadakane, *Z. Anorg. Allg. Chem.* 2021, **647**, 1930-1937.
- [3] N. C. Sukmana, Sugiarto, J. Shinogi, A. Yamamoto, A. Higashiura, T. Sakaguchi, M. Sadakane, *Eur. J. Inorg. Chem.* 2022, **2022**, e202200322.

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Research keywords: Polyoxometalate, Metal nanocluster, Catalysis


Metal Nanoclusters within Polyoxometalates

Metal nanoclusters have attracted increasing interest in diverse fields, including catalysis, energy conversion, and sensing, owing to their properties that are dependent on their structures, electronic states, and supporting ligands. However, they frequently suffer from their instability, unfavorable agglomeration, and decomposition during use. Polyoxometalates (POMs) are bulky anionic metal-oxo clusters possessing unique structures and properties, such as acidity/basicity, electronic states, and redox properties. Our group has recently developed synthetic methods for metal-oxo clusters, inorganic–organic hybrids, and supported metal catalysts using POMs as multidentate inorganic ligands.¹⁻³ Here, we present a new strategy for synthesizing highly durable and reactive metal nanoclusters with their distinctive catalytic properties by utilizing POMs as multidentate metal oxide ligands.⁴⁻⁶



References.

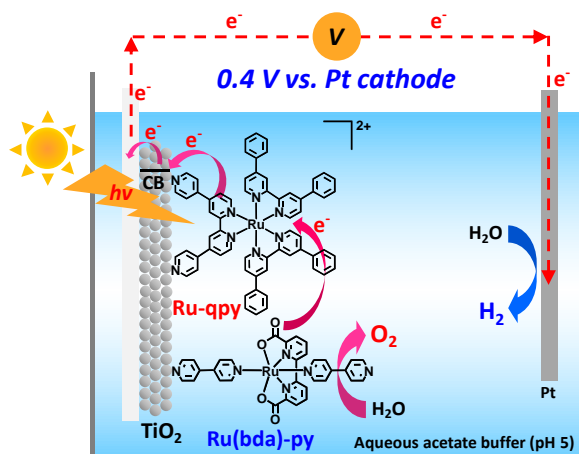
- [1] C. Li, N. Mizuno, K. Yamaguchi, K. Suzuki, *J. Am. Chem. Soc.* **2019**, *141*, 7687. [2] T. Minato, D. Salley, N. Mizuno, K. Yamaguchi, L. Cronin, K. Suzuki, *J. Am. Chem. Soc.* **2021**, *143*, 1289. [3] K. Xia, T. Yatabe, K. Yonesato, T. Yabe, S. Kikkawa, S. Yamazoe, A. Nakata, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205873. [4] K. Yonesato, H. Ito, H. Itakura, D. Yokogawa, T. Kikuchi, N. Mizuno, K. Yamaguchi, K. Suzuki, *J. Am. Chem. Soc.* **2019**, *141*, 19550 [5] K. Yonesato, S. Yamazoe, D. Yokogawa, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2021**, *60*, 16994. [6] K. Yonesato, D. Yanai, S. Yamazoe, D. Yokogawa, T. Kikuchi, K. Yamaguchi, K. Suzuki, *Nat. Chem.* **2023**, *15*, 940.

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Research keywords: Artificial Photosynthesis, Photoelectrochemistry, Photocatalysis, Coordination Compounds, Semiconductors


Molecular-Based Photoanodes for Photoelectrochemical Overall Water Splitting

Photoelectrochemical overall water splitting by the semiconductor electrodes modified with functional molecules has attracted considerable attention in recent years. Here we report a highly efficient and stable molecular-based TiO₂ photoanode modified with both a polypyridyl ruthenium photosensitizer (**Ru-qpy**)^[1] and a Ru(bda)-type water oxidation catalyst (WOC) (**Ru(bda)-py**) by our “pyridyl anchoring technique”^[2]. A photoelectrochemical cell consisting of this photoanode and a Pt cathode shown below promotes overall water splitting with the second highest solar-to-hydrogen conversion efficiency (0.07%) only by giving a small extra electrical bias (0.4 V).^[3] The photocatalytic performance of a molecular-based photoanode using a Co polyoxometalate as a WOC will be also discussed.^[4]



Reference.

- [1] K. Morita, K. Sakai, H. Ozawa, *ACS Appl. Energy Mater.*, **2019**, *2*, 987.
- [2] K. Takijiri, K. Morita, T. Nakazono, K. Sakai, H. Ozawa, *Chem. Commun.*, **2017**, *53*, 3042; K. Morita, K. Takijiri, K. Sakai, H. Ozawa, *Dalton Trans.*, **2017**, *46*, 15181; H. Ozawa, K. Sakai, *AsiaChem Magazine*, **2021**, *2*, 80.
- [3] X. Yan, K. Sakai, H. Ozawa, *ACS Catal.*, **2023**, *13*, 13456.
- [4] Y. Tomita, N. Taira, K. Sakai, H. Ozawa, *in preparation*.

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Research keywords: Hybrid Organic-Inorganic Polyoxometalates, Redox chemistry, Electrochemistry, Nano-encapsulation, Ion Transport.


Monitoring proton transport through single-layer carbon to encapsulated POMs

Molecular metal oxides have received considerable attention in recent years as potential components in future energy storage devices thanks to their structural stability and rapid, reversible redox properties. Due to their discrete nature, their use as components in energy storage devices relies on their stable combination with conductive solid or liquid-phase supports. We have been developing a range of cluster-based redox materials and exploring their potential application in a range of technologies.

We recently showed that molecular metal oxide encapsulation within the cavities of single-walled carbon nanotubes leads to host-guest redox materials with exceptional long-term cycle stability.^[1,2,3] Our recent studies have focussed on how counterions can access encapsulated POMs, leading to new understanding in energy storage and electrocatalysis of small molecules.^[4]

References.


- [1] Jordan, J. W., Lowe, G. A., McSweeney, R. L., Stoppiello, C. T., Lodge, R. W., Skowron, S. T., Biskupek, J., Rance, G. A., Kaiser, U., Walsh, D. A., Newton, G. N., Khlobystov, A. N., *Adv. Mater.* **2019**, *31*, 1904182.
- [2] Jordan, J. W.; Cameron, J. M.; Lowe, G. A.; Rance, G. A.; Fung, K. L. Y.; Johnson, L. R.; Walsh, D. A.; Khlobystov, A. N.; Newton, G. N. *Angew. Chem. Int. Ed.*, **2022**, *61*(8): e202115619.
- [3] Jordan, J. W.; Fung, K. L. Y.; Skowron, S. T.; Allen, C. S.; Biskupek, J.; Newton, G. N.; Kaiser, U.; Khlobystov, A. N. *Chem. Sci.*, **2021**, *12*, 7377–7387.
- [4] Jordan, J. W.; Mortiboy, B. Khlobystov, A. N.; Johnson, L. R.; Newton, G. N.; Walsh, D. A. *J. Am. Chem. Soc.* **2023**, *145*, 16, 9052–9058

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Research keywords: polyoxometalates; synthesis; reactivity; non-aqueous speciation; mechanochemistry; super-reduction; catalysis

Progress towards general, versatile and scalable methods for synthesising reactive / electron-rich polyoxometalates

The range of polyoxometalates (POMs) that are used commercially on a large scale remains rather limited and their preparation generally relies on historical, well established aqueous methods. POM chemistry has seen major advances over the last forty years, but if these are to translate to *e.g.* catalysts for major processes or materials for new technologies then straightforward, reliable and scalable synthetic methods are needed. Using non-aqueous approaches, we have expanded the range of heterometallic Lindqvist-type POMs and explored rational chemical reduction methods in order to develop new POM reactivity and have now turned our attention to optimising our synthetic procedures with a view to scalability. This talk will highlight recent advances and give examples of improved procedures that facilitate access to new families of reactive POMs.

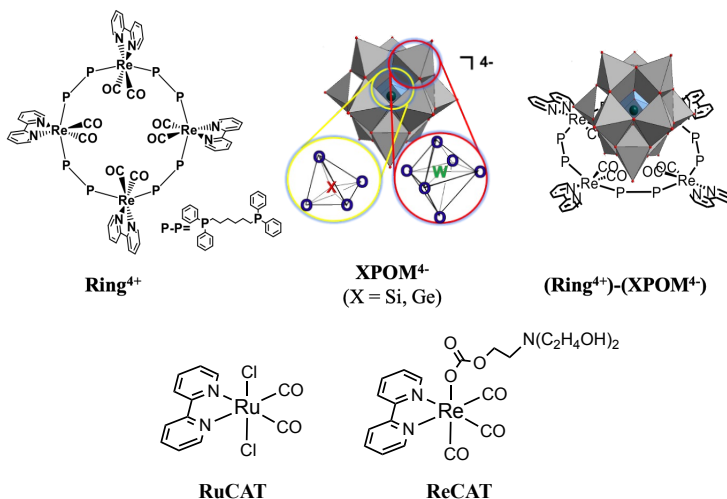
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Research keywords: photocatalytic CO₂ reduction, photosensitizer, Keggin-type POM, ring-shaped Re(I) tetranuclear complex

Supramolecular multi-electron redox photosensitisers comprising a ring-shaped Re(I) tetranuclear complex and a polyoxometalate

Redox reactions initiated by photochemical electron transfer have been widely used in various research fields, such as organic synthesis and artificial photosynthesis.^[1]

In this presentation, we report new redox PSs of 1:1 supramolecules ((**Ring** that comprise a ring-shaped Re(I) tetranuclear complex with 4+ charges (**Ring**⁴⁺) and a Keggin-type heteropolyoxometalate with 4- charges (**XPOM**⁴⁻).^[2] These PSs photochemically accumulate multi-electrons in one molecule (three or four electrons) in the presence of an electron donor and can supply electrons with different reduction potentials. PSs were successfully applied in the photocatalytic reduction of CO₂ using catalysts (Ru(II) and Re(I) complexes) and triethanolamine as a reductant. In photocatalytic reactions, these supramolecular PSs supply a different number of electrons to the catalyst depending on the redox potential of the intermediate, which is made from the one-electron-reduced species of the catalyst and CO₂. Based on these data, information on the reduction potentials of the intermediates was obtained.



Reference.

[1] "Photocatalytic reduction of CO₂ using metal complexes", Y. Yamazaki, H. Takeda, O. Ishitani, *J. Photochem. Photobiol. C*, **2015**, 25, 106-137 <http://dx.doi.org/10.1016/j.jphotochemrev.2015.09.001>.

[2] "Supramolecular multi-electron redox photosensitisers comprising a ring-shaped Re(I) tetranuclear complex and a polyoxometalate", M. Takahashi, T. Asatani, T. Morimoto, Y. Kamakura, K. Fujii, M. Yashima, N. Hosokawa, Y. Tamaki, O. Ishitani, *Chem. Sci.* **2023**, 14, 691-704 [10.1039/d2sc04252e](https://doi.org/10.1039/d2sc04252e).

Introduction of a chemical protection group in the synthesis of polyoxometalates

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One of the most simple coordination complexes, hexa-aqua transition metal ions, $[M(H_2O)_6]^{n+}$, have a multiple degree of freedom in geometrical parameters; the distortion along an axial direction, the Jahn-Teller distortion caused by the ligand field effect, or a distortion from an ideal octahedron by the effect from the crystal packing. In addition to the displacements of six oxygen atoms, the rotations of the aqua ligands along the M–O axis allow an additional freedom of orientations of the ligands. These various orientations and distortions may be the cause of the para-magnetism due to the prohibition of an alignment of an exact axis in the crystal packing. If we can force to line the ion up in an arrangement like in an oxide cell such as the perovskite lattice, even the simplest complexes may exhibit an important function by the ordering of a crystal axis for future functional materials. We have been investigating such an oxide relevant supporting complexes of polyoxocations¹, FeMo cofactor mimicking cation complexes², and Ti^{4+} cation complexes³. In this symposium, by using a robust ligand with three fold axis, 1,4,7-triazacyclononane, we explored the chemical protection group methodology in the synthesis of inorganic chemistry. In organic chemistry, various synthetic techniques are available such as an idea of good to bad leaving groups and chemical protection groups for a specific reaction. In polyoxometalate synthesis, it may be a welcome addition to introduce the idea of chemical protection groups and it will lead us to the unexplored species in solution. Without an introduction of a proper chemical protection group, the polymerization reaction of polyoxometalates in the solution may be in a self-assembled process and a specific reaction to produce a particular dimers, trimers and tetramers separated from the equilibrium may be achieved.

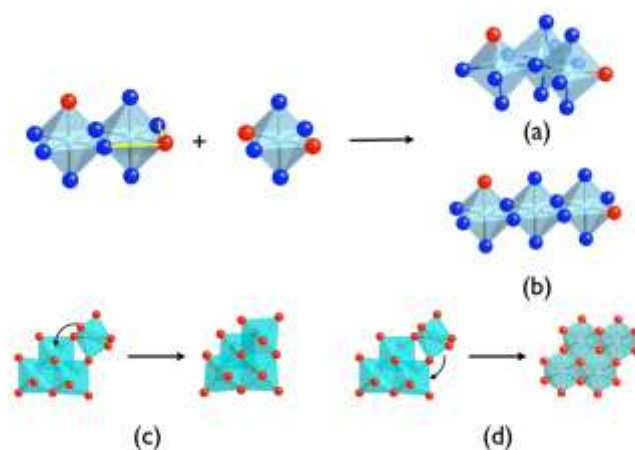


Figure 1. Condensation reaction from a dimer to trimers (a) a bending dimer structure, (b) Straight dimer structure., Condensation reaction of trimers to tetramers (c) a bending structure, (d) a planer structure.

(1) Sugiarto; Tagami, T.; Kawamoto, K.; Hayashi, Y. *Dalton Trans.* **2018**, 47, 9657–9664.

(2) Sugiarto; Kawamoto, K.; Hayashi, Y. *J. Inorg. Biochem.* **2019**, 201, 110821.

(3) Sugiarto; Kazakami, S.; Kawamoto, K.; Hayashi, Y. *Inorg. Chim. Acta* **2020**, 509, 119691.

Redox molecules in next-generation batteries

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Lithium-ion batteries have delivered a revolution in portable electronics and have begun to unlock electrification of the automotive industry. However, intrinsic performance limitations mean that many applications will be out of reach for lithium-ion technology. We must explore alternatives if we are to have any hope of meeting the long-term needs for energy storage. The NAMI group is focused on tackling the underpinning chemical and materials challenges within next-generation energy devices and in particular batteries.

Replacing the heavy transition metal oxide at which the Li^+ ions and electrons are stored in li-ion cells, with a light weight lithium oxide or sulphide is a promising strategy to achieve a higher energy batteries. For example, the Li-air (O_2) battery has a theoretical specific energy of 3600 Wh kg^{-1} , thus significantly exceeding that of Li-ion, but many hurdles hinder its realization. One of the major challenges is due to the need to electrochemically form and decompose solid insulating active materials which often results in early cell death, low capacity and limited power. Here, we discuss recent advances made in our labs to combat these problems using soluble redox molecules that are able to promote longer discharge and improve the kinetic for oxygen and sulfur electroreduction. We show that these molecules can shuttle electrons from the electrode to the insulating active material, thereby overcoming the intrinsic limitations of the cell design. We use electrochemical methods to analyse the reaction mechanism by which redox mediators operate and explore the use of polyoxometalates as potential redox mediators in these batteries.



Lee Johnson received his first degree from Newcastle University, after which he completed a PhD and post-PhD Fellowship in physical chemistry and electrochemistry at the University of Nottingham. He then joined the research group of Prof Sir P.G. Bruce FRS at the University of Oxford, where he studied the elementary processes taking place within the lithium- O_2 battery. In 2017, he was awarded a Nottingham Research Fellowship, University of Nottingham, followed by an EPSRC Fellowship in 2018, both to support study of next-generation batteries. In 2019 he was promoted to Associate Professor in the School of Chemistry. His current research interests focus on understanding interfacial reactions, degradation, and charge transfer, in electrochemical energy devices.

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Research keyword: New polyoxometalates; Assembly of Polyoxometalate; Polyoxometalate based metal oxide.

IMPOMs progress in Japan

Although 2020 and 2021 activities were completely stopped by COVID-19, we could achieve following young researchers exchange programs.


2019: 1) A master course (Prof. Paul, Centrale de Lille) visited our lab. for 3 months. 2) A PhD student (Prof. Streb, Ulm Uni.) visited Prof. Hayashi group for 2 months, 3) A master student (Hiroshima Uni.) visited Prof. Errington group for 2 months. 4) A master student (Hiroshima Uni.) visited Prof. Paul group for 2 months. 5) A PhD student visited summer school at Newcastle Uni.

2020, 2021:

2022: 1) A PhD student (Prof. Streb, Ulm Uni.) visited Prof. Hayashi group for 2 months, 2) A master student (Prof. Paul, Centrale de Lille) visited our lab. for 6 months. 3) A master student (Prof. Nishihara, Hiroshima Uni. visited Prof. Lee lab for 3 months. 4) A PhD student (Prof. Sakai, Kyusyu Uni.) did lab-tour (Bremen, Mainz, Sorbonne, Nottingham, Glasgow), 5) An assistant prof. (Hiroshima Uni.) did lab-tour (Nottingham and Newcastle). 6) Four master students and two assistant profs. (Hiroshima Uni. and Kyusyu Uni.) joined Electrochemistry workshop at Newcastle Uni.

2023: 1) A master course student (Hiroshima Uni.) is visiting Prof. Kortz group for 3 months.

Until now, we (Japanese members) published 110 papers including 9 INPOMs collaboration papers until April 2023. Papers with exchange students are [1] T. Iwano, K. Shitamatsu, N. Ogihara, M. Okuno, Y. Kikukawa, S. Ikemoto, S. Shirai, S. Muratsugu, P. Waddell, R. J. Errington, M. Sadakane, S. Uchida, *ACS Appl. Mater. Inter.* **2021**, *13*, 19138. [2] K. Shitamatsu, T. Kojima, P. G. Waddell, Sugiarto, H. E. Ooyama, R. J. Errington, M. Sadakane, *Z. anorg. allgem. Chem.* **2021**, *647*, 1239. [3] S. Repp, K. L. Junginger, D. Sorsche, T. Zorn, A. Poeppler, Y. Kikukawa, Y. Hayashi, C. Streb, *Dalton Trans.* **2023**, *52*, 4002. [4] K. S. Vargas, J. Zaffran, M. Araque, M. Sadakane, B. Katryniok, *Mol. Catal.* **2023**, *535*, 112856.

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Research keywords: single-molecule, transistor, non-volatile memory, dielectrics

Concept and Fabrication of Non-Volatile Memory on Single-Molecule Electret

Ferroelectric materials which have switchable spontaneous polarization by an external electric field, have been applied as non-volatile memory devices such as IC cards. However, these types of material have the limitation of minimalization, and their memory properties tend to disappear with decreasing the size to less than 10~100 nm.

Recently, our group developed ferroelectric-like novel memory materials using a single-molecule of terbium-ion encapsulated Preyssler-type polyoxometalate (POM), $[\text{Tb}^{3+} \text{---} \text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$.^[1] This type of POM has cage-like molecular frameworks and one metal ion is encapsulated in either two stable ion sites within a molecular cage. From this point of view, POM showed molecular polarization depends on the position of encapsulated metal ion, and this polarization can be switched by position shifts of metal ion within sites. Applying an external electric field to this POM, the ion movement between two stable ion sites was generated, and ferroelectric-like polarization hysteresis was observed. This ferroelectric-like memory function in a single-molecule was named as single-molecule electret (SME). The SME are expected to be used for ultra-high-density non-volatile memory because of the almost 1 nm minimalization limitation of single-molecule. In this work, we fabricated a field-effect transistor with SME, and fundamental memory properties such as V_{GS} - I_{DS} properties were evaluated.

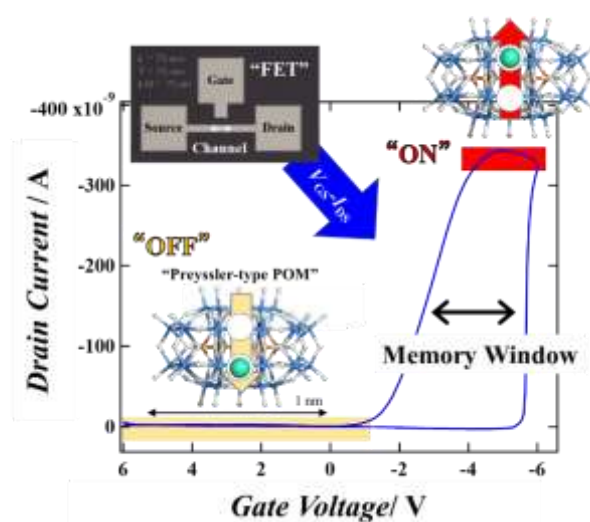



Fig.1. Molecule structure and memory properties of Preyssler-type polyoxometalates.

Reference.

[1] C. Kato, S. Nishihara, *et al.*, *Angew. Chem. Int. Ed.*, **2018**, 57, 13429-13432.

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Research keywords: Single-Molecule electret, Semiconductor, Memory Device

Memory device applications of Single-Molecule electret for business development

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In the advanced information society, reducing the power consumption of computers is a major social issue. A new type of computing based on nonvolatile memory has been proposed as a solution, but there is no memory material that satisfies the required performance. Against this backdrop, Professor Sadafumi Nishihara of Hiroshima University has succeeded in developing an innovative memory material, "Single-Molecule Electret," paving the way for the realization of this new type of computing.

Our company is a start-up established based on the seeds of this technology. In this project, we manufacture and sell Single-Molecule Electret and license out the technology for device implementation, mainly for memory. In this presentation, we will present the background of the device development and an overview of the business.

Reference.

[1] S. Nishihara, *et al.*, *Angew. Chem. Int. Ed.*, **2018**, *57*, 13429-13432.

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Research keywords: Artificial Photosynthesis, Cobalt Complex, Hydrogen Evolution, NHC Ligand

Molecular Catalysis in H₂ and O₂ Evolution from Water

Artificial photosynthesis based on splitting water into H₂ and O₂ with solar energy has attracted recent years. In order to realize overall water-splitting reaction ($2\text{H}_2\text{O} + 4h\nu \rightarrow 2\text{H}_2 + \text{O}_2$) on the basis of molecular systems, it is crucial to ensure sufficient driving force for both H₂ and O₂ evolution reactions (HER and OER). We have previously studied on molecular photosystems in which HER is driven by oxidative quenching of $[\text{Ru}^*(\text{bpy})_3]^{2+}$, but the reaction rates and turnover numbers were relatively low when **Co-NHC1** and other molecular catalysts were employed.^{1,2} On the other hand, the reductive quenching of $[\text{Ru}^*(\text{bpy})_3]^{2+}$ provides large driving force for HER but insufficient driving force for OER in the acidic to neutral pH range. In this study, we focus on a new strategy to maintain the driving force for both HER and OER by carrying out the reductive quenching process of $[\text{Ru}^*(\text{bpy})_3]^{2+}$ under highly alkaline conditions.

A large amount of H₂ (TON = 40000 at pH = 12.8) evolved when using a $[\text{Ru}(\text{bpy})_3]^{2+}$ /ascorbate photochemical system in the presence of a newly synthesized new Co-NHC catalyst for HER even under highly alkaline conditions (Figure 1). Furthermore, it was found that the new catalyst is more durable than **Co-NHC1**. More interestingly, as the pH is increased, sustained evolution of H₂ takes place in larger amounts (pH < 12.8). We have recently started to study OER in alkaline media catalyzed by Co-POM³ and other metal complexes.

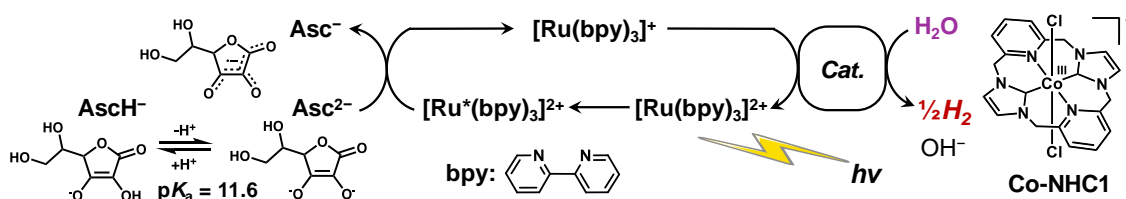



Figure 1. Photochemical hydrogen evolution from alkaline water.

References.

- [1] Kawano, K.; Yamauchi, K.*; Sakai, K.*, *Chem. Commun.* **2014**, 50, 9872-9875.
- [2] Yatsuzuka, K.; Yamauchi, K.*; Kawano, K.; Ozawa, H.*; Sakai, K.*, *Sustainable Energy Fuels* **2021**, 5, 740-749.
- [3] Taira, N.; Yamauchi, K.; Sakai, K.*, *ACS Catal.* **2023**, 13, 3211-3223.

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Research keywords: Magnetism, Copper(II), $S=1/2$, Keggin-type tungstate,

Magnetic relaxation phenomena of $S=1/2$ copper(II)-substituted Keggin-type Polyoxotungstates

Recently, mononuclear $S=1/2$ first-row transition metal systems carrying less abundant nuclear spin organic ligands have been investigated as a potential molecular spin qubit for quantum computation [1]. The molecular metal oxides or polyoxometalates also become a good candidate for electronic spin qubit material since some of them have less abundant nuclear-spin ligand skeletons [2]. In this presentation, magnetic properties of an $S=1/2$ copper(II)-substituted Keggin-type silicotungstate [$(n\text{-C}_4\text{H}_9)_4\text{N}$] $_4\text{H}_2[\text{SiW}_{11}\text{O}_{39}\text{Cu}]$ (**1**) and its related compounds are reported [3].

The continuous-wave electron spin resonance spectrum for **1** showed four hyperfine signals between 250 to 280 mT at room temperature. This is characteristic of the interaction between the nuclear spin ($^{63,65}\text{Cu}$, $I=3/2$) and the electronic spin of copper ions. The extracted g value ($g_{\parallel}=2.343$, $g_{\perp}=2.069$) and hyperfine splitting value A ($A_{\parallel}=12.68$ mT, $A_{\perp}=1.0$ mT) indicate five-coordinated square-pyramidal coordination geometry around the copper atom [4].

Ac magnetic susceptibility measurements for magnetically diluted **1**, [$(n\text{-C}_4\text{H}_9)_4\text{N}$] $_4\text{H}_2[\text{SiW}_{11}\text{O}_{39}\text{Cu}_{0.05}\text{Zn}_{0.95}]$ (**dil.1**) showed the out-of-phase signals in an applied static magnetic field (H_{dc}) and low temperatures (Figure 1). This indicates the slow magnetic relaxation of this compound. Discussion of the relaxation mechanism of this compound and relaxation behaviors of other related compounds will be reported.

A part of this work was conducted at the Institute for Molecular Science (JPMXP1222MS1035 and JPMXP1223MS1054). We also acknowledge JSPS KAKENHI (23K13769) and the Core-to-Core program (International Network in Polyoxometalate Science for Advanced Functional Energy Materials).

Reference.

- [1] D. E. Freedman *et al.*, *J. Am. Chem. Soc.*, **2014**, *136*, 15841.
- [2] A. Gaita-Ariño *et al.*, *J. Am. Chem. Soc.*, **2008**, *130*, 8874.
- [3] T. Ishizaki and T. Ozeki, *Dalton Trans.*, **2023**, *52*, 4678.
- [4]. A. M. V. Cavaleiro *et al.*, *Polyhedron*, **1999**, *18*, 1163.

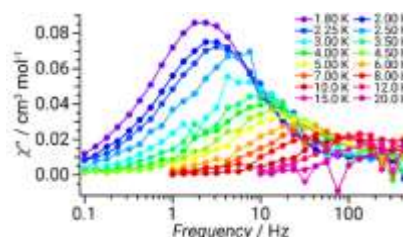



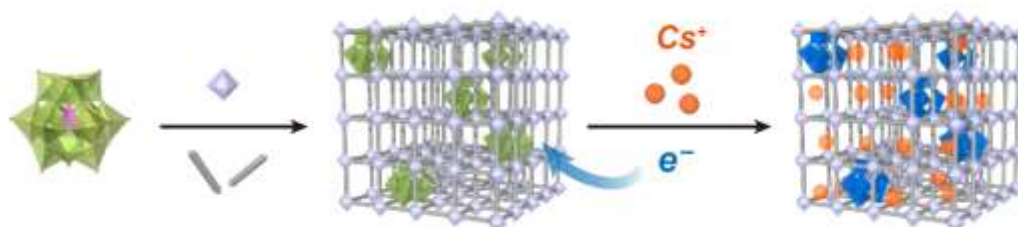
Figure 1 The out-of-phase signals of **dil.1** measured in $H_{\text{dc}}=3000$ Oe.

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Research keywords: metal–organic frameworks • ion capture • redox • porous materials

Reduction-Induced Uptake of Cs⁺ in Metal–Organic Frameworks Loaded with Polyoxometalates

Materials for Cs⁺ adsorption continue to be important for the treatment of various solutions. Metal–organic frameworks (MOFs) with large specific surface areas promise adsorption properties for various gases, vapors, and ions. However, the utilization of MOFs for Cs⁺ capture is still in its infancy. To address this issue, we hybridized a MOF with a polyoxometalate (POM), which is an anionic metal–oxo cluster with ion exchangeable counterions. In particular, the composite of ZIF-8 and [α-PMo₁₂O₄₀]³⁻ (**PMo₁₂/ZIF-8**) adsorbed Cs⁺ ions effectively by ion-exchange with the counter cations of POM, whereas the Cs⁺ adsorption by pristine ZIF-8 was negligible. In addition, the reduction of Mo within the POM from Mo^{VI} to Mo^V by ascorbic acid during the Cs⁺ uptake process doubled the Cs⁺ uptake capacity of **PMo₁₂/ZIF-8**. This observation can be attributed to the increased overall negative charge of POM facilitating the Cs⁺ uptake to compensate for the charge imbalance. Besides, hybridization with other MOFs (MIL-101 and UiO-66) largely suppressed the Cs⁺ uptake, highlighting the importance of hydrophobicity in Cs⁺ capture. Furthermore, **PMo₁₂/ZIF-8** led to an outstanding Cs⁺ uptake (291.5 mg g⁻¹) with high selectivity (79.6%) from quinary mixtures of alkali metal cations among representative porous materials (Prussian blue and zeolites).



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Research keywords: (hydrogel, polymer, separation, chemical engineering)

Stability of Hydrogel as Carriers of Phosphotungstic Acid as a Heterogeneous Catalyst

Introduction: The Keggin-type phosphotungstic acid $H_3PW_{12}O_{40}$ (PTA) has high levels of acidity and thermal stability, that makes it widely used as a solid catalyst in gas phase or as a homogeneous catalyst in liquid phase¹⁾. Unfortunately, PTA readily dissolve in polar solvents, rendering it less useful as homogeneous catalyst. In this research, a novel technique is proposed to synthesize a heteropoly acid supported composite and its stability as a catalyst was also tested.

Results and Discussion: A PTA composite was synthesized via radical polymerization by mixing Triethylene Glycol Methyl Ether Methacrylate (TEGMA) with PTA²⁾. Figure 1 indicated the FT-IR spectra of TEGMA gel, pure PTA and PTA/TEGMA composites. The absorption peak of composites located at 1081 cm^{-1} is the characteristic absorption of the P-O bond. The absorption peak at 802 cm^{-1} , corresponding to the vibration band of W-O in PTA, becomes sharper and shifts to 819.6 cm^{-1} (for 40wt% PTA/TEGMA composite), implying the hydrogen bonding interaction between PTA and TEGMA. These results demonstrate that the hydrogen bonding between PTA and TEGMA can guarantee the stability of PTA at a comparatively high concentration in the composites. The suitability of the PTA/TEGMA composite as was performed via leaching tests and catalytic experiments. Figure 2 displayed the amount changes of ethyl acetate over time with synthesized and 2 times washed 40wt% PTA/TEGMA composites. The solid line was before filtering composites from solution and the dotted line was after filtering. It demonstrated that the synthesized and washed composites had the similar curves, indicating the acid activity of composites did not decrease with the immersing time. It signified that the reaction can be controlled through adding or filtering the composite, more convenient than using the pure PTA for the reaction.

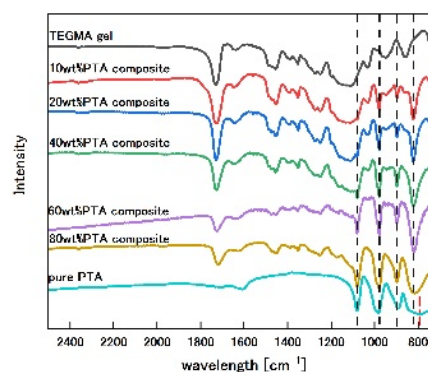


Fig.1 FT-IR patterns of TEGMA gel, pure PTA and PTA/TEGMA composites

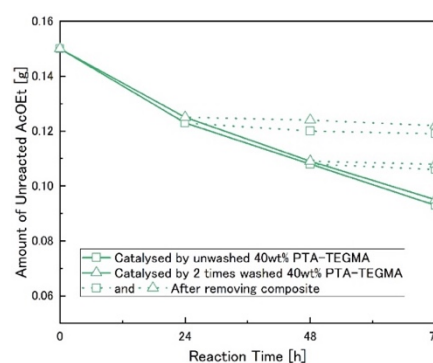



Fig.2 Weight changes of AcOEt catalyzed by 40wt% PTA/TEGMA composites

Conclusion: The PTA was successfully immobilized in hydrogel and could react as a solid acid catalyst in water.

References

- 1) Kozhevnikov, I.V., *Chem. Rev.* 1998, **98**, 171-198, 2) Zhu, J. *et al. Materials Advances* 2021, **2**, 3556-3559

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Research keywords: Polyoxothiometalate, Substitution reactions

Synthesis of polyoxothiometalates


Metal sulfides exhibit unique physicochemical properties that differ from those of metal oxides. Interestingly, even the addition of sulfur as dopant to metal oxides leads to drastic changes in their properties and applications.^[1] Therefore, they attract widespread interest in diverse fields of chemistry including photochemistry, catalysis, sensing, and electronics.

Polyoxometalates (POMs) exhibit unique acidity/basicity, redox, photochemical, and electrochemical properties that strongly depends on their constituent element, composition, arrangement, and electronic state. Importantly, the metal sites of POMs can be substituted with a variety of types, numbers, and arrangements of metal atoms, making them fascinating candidates for the development of various functional molecular materials. Therefore, we envisaged that the substitution of oxygen sites of POMs will impart the unique acidity/basicity, redox, photochemical, and catalytic properties, leading to the development of unprecedented properties and applications of the polyoxothiometalates (POTMs). To date, the oxygen sites of POMs could be replaced by various organic ligands (e.g., organophosphate, organosilicate, alkoxide, imide, and pyridines) *via* dehydration condensation or ligand-exchange reaction with aqua ligands of POMs.^[2] On the other hands, it is still limited to a few reports of substitution with sulfur atoms, hindering the exploration of properties and applications of POTMs. Therefore, it remains challenging task to develop facile and versatile method for the synthesis of POTMs by direct induction from parent POMs.

Recently, we develop a novel synthetic method for polyoxothiometalate based on the substitution reaction of oxygen atoms of POMs with sulfur atoms. Under the modified synthetic conditions, the site-selective O/S substitution proceeded in a one-step reaction of the precursor POMs and sulfurizing reagents without undesirable decomposition/aggregation. In the presentation, the synthetic method, structures, electronic states, and properties of the polyoxothiometalate will be discussed in detail.

[1] a) Y. Liu, W. Wang, X. Xu, J.-P. M. Veder, Z. Shao, *J. Mater. Chem. A* **2019**, *7*, 7280–7300; b) Y. Zhu, X. Liu, S. Jin, H. Chen, W. Lee, M. Liu, Y. Chen, *J. Mater. Chem. A* **2019**, *7*, 5875–5897.

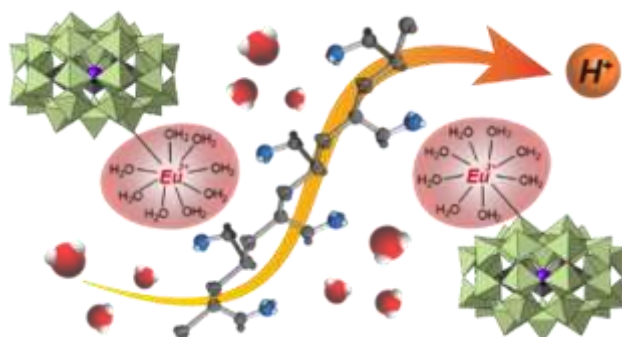
[2] a) J. Breibeck, N. I. Gumerova, A. Rompel, *ACS Org. Inorg. Au* **2022**, *2*, 477–495; b) A. Jimbo, C. Li, K. Yonesato, T. Ushiyama, K. Yamaguchi, K. Suzuki, *Chem. Sci.* **2023**, *14*, 10280–10284.

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Research keywords: Ionic crystals, Preyssler-type POMs, Hydrogen bonding network, Proton conduction


Effect of Incorporated Polymer Species toward Proton Conduction in Inorganic Frameworks Based on Eu-Bonded Preyssler-Type Phosphotungstates

Polyoxometalates (POMs), which are nano-sized anionic metal-oxygen clusters, can efficiently transport protons because of the small surface charge density. In particular, Keggin-type POMs (e.g. $[\text{PW}_{12}\text{O}_{40}]^{3-}$) have been considered as candidates of solid proton conductors. However, application of Keggin-type POMs has been limited because of dissolution under high temperature and humidified conditions. To overcome this problem, Our group has developed crystalline composites based on Preyssler-type POMs ($[\text{X}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{(15-n)-}$)^[1] which has higher acidity than Keggin-type POMs and polymers^{[2],[3]}. In this work, we focused on Eu-bonded Preyssler-type POMs ($\text{Eu}[\text{KP}_5\text{W}_{30}\text{O}_{110}]^{11-}$; **EuK**)^[4], for enhanced proton conductivity. By utilizing these POMs, it is expected to attract water molecules around Eu ion which can contribute to high proton conductivity. According to these considerations, we synthesized the crystalline composites based on Eu-bonded Preyssler-type POMs (**EuK**), potassium ion and polymers (poly(allylamine) (PAA) and poly(vinylalcohol) (PVA)), which are abbreviated as **EuK-PAA** and **EuK-PVA**. By utilizing these compounds, we investigated the effect of the kind of polymers toward proton conduction. As a result, high proton conduction under only highly-humidified condition (relative humidity (RH) 90%) was achieved in **EuK-PAA** while high proton conduction under mildly-humidified condition (RH 75%) was maintained in **EuK-PVA**.



[1] S. Sun *et al.*, *Polyhedron* **169**, 84 (2019). [2] K. Niinomi *et al.*, *Inorg. Chem.*, **56**, 15187 (2017).

[3] T. Iwano *et al.*, *Commun. Chem.*, **2**, 1 (2019). [4] T. Iwano *et al.*, *ACS Appl. Mater. Interfaces*, **13**, 19138 (2021).

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Research keywords: hetero-multinuclear metal clusters, polyoxometalates, stepwise synthesis

Conjugation of hetero-multinuclear metal–oxo clusters within polyoxometalates

Precise structural design of large hetero-multinuclear metal–oxo clusters is crucial for controlling their large spin ground states and multielectron redox properties for application as a single-molecule magnet, molecular magnetic refrigeration, and efficient redox catalyst. However, it is difficult to synthesize large hetero-multinuclear metal oxo clusters as designed because the final structures are unpredictable when employing conventional one-step condensation reaction of metal cations and ligands. In this presentation, a “cationic metal glue strategy” for increasing the size and nuclearity of hetero-multinuclear metal–oxo clusters by using lacunary-type anionic molecular metal oxides (polyoxometalates) as rigid multidentate ligands is reported.^[1] Conjugation of $\{MMn_4\}$ ($M = Fe, Mn$) oxo clusters with Mn and/or Ln ($Ln = Gd, Tb, Dy, Lu, \text{ and } Ce$) as “glues” enabled the synthesis of large hetero-multinuclear metal–oxo clusters with 14 metal cations in a predictable way (Figure 1).

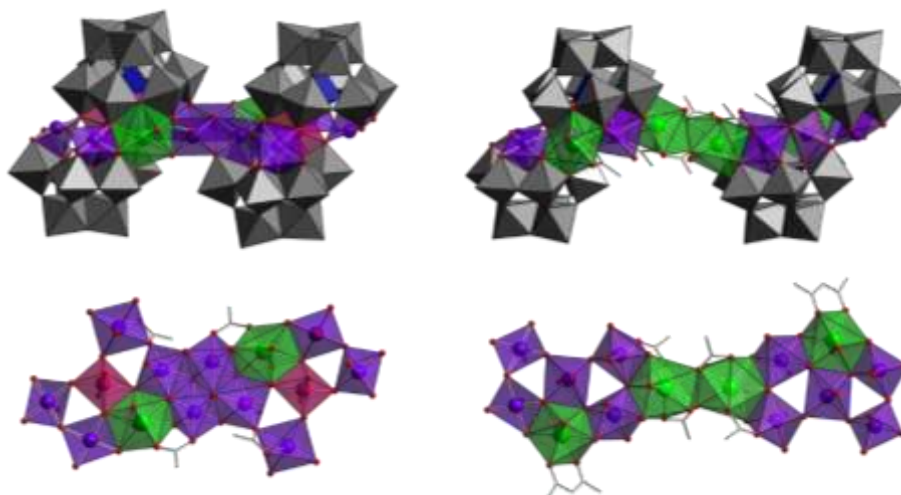
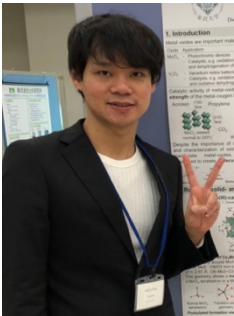


Figure 1. Conjugated large hetero-multinuclear metal–oxo clusters and respective core structures.

Reference

[1] Takuo Minato, Masahiro Sadakane, *Angew. Chem. Int. Ed.* **2023**, e20230946.

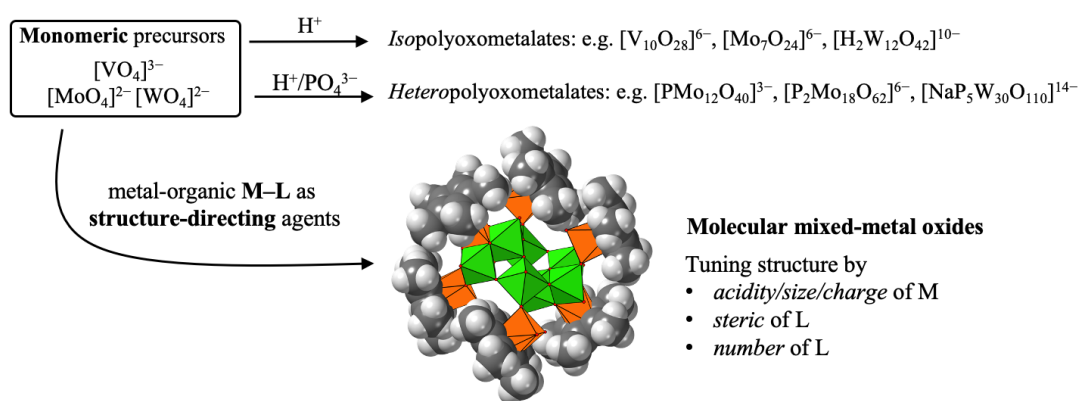
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Research keywords: aqueous chemistry, polyoxometalate, organometallic, X-ray crystallography

Synthesis and structural transformation of organometallic-polyoxometalates

"In this way we should have some control over the reaction through the number of vacant sites, the size of the nonlabile ligand, and the metal ion charge of the Lewis acidic coordination compound."
(Isobe and Yagasaki, *Acc. Chem. Res.*, **1993**, 524–529)


My research focuses on the synthesis of new molecular mixed-metal oxides using metal-organic complexes to guide the condensation of monomeric VO_4^{3-} , MoO_4^{2-} , or WO_4^{2-} oxyanions in aqueous solution (Scheme 1). In this context, I present our ongoing work on "*polyoxo-organometals*", a term I coined to describe a class of molecular organometallic oxides formed by merging organometallic cations into a polyoxometalate backbone.^[1] Two topics are presented: (i) systematic synthesis of polyoxo-(C_6H_6)Ru and (ii) structural transformation of polyoxo-(C_5Me_5)Ir^[2] in alcohols. The take-home messages are crystallization temperature is crucial to obtain pure polyoxo-(C_6H_6)Ru clusters and structural transformation of polyoxo-organometals is potentially relevant to the surface dynamics of heterogeneous catalysts during catalysis.



Scheme 1. Metal-organic-directed self-assembly of mixed-metal oxide clusters.

References

- [1] P. Putaj, F. Lefebvre, *Coord. Chem. Rev.* **2011**, 255, 1642–1685.
 [2] Sugiarto, J. Shinogi, M. Sadakane, *Inorg. Chem.* **2023**, 62, 6759–6767.

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Research keywords: alkylammonium polyoxometalates, thermal transformation

Synthesis, characterization, and thermal transformation of alkylammonium isopolymolybdates

We present that several alkylammonium polyoxometalates were prepared by reactions of metal oxides in aqueous alkylamine solution and subsequent heating (Figure 1). Methylammonium monomolybdate, $(\text{CH}_3\text{NH}_3)_2\text{MoO}_4$ was prepared by dissolving MoO_3 in an aqueous methylamine solution and subsequent addition of N,N-dimethylformamide (DMF). Solid state heating of the $(\text{CH}_3\text{NH}_3)_2\text{MoO}_4$ in air released water and methylammonium to produce several methylammonium isopolymolybdates such as $(\text{CH}_3\text{NH}_3)_8[\text{Mo}_7\text{O}_{24}-\text{MoO}_4]$, $(\text{CH}_3\text{NH}_3)_6[\text{Mo}_7\text{O}_{24}]$, $(\text{CH}_3\text{NH}_3)_8[\text{Mo}_{10}\text{O}_{34}]$, and $(\text{CH}_3\text{NH}_3)_4[\text{Mo}_8\text{O}_{26}]$, and molybdenum oxides such as hexagonal MoO_3 and orthorhombic MoO_3 which were confirmed by single crystal XRD, powder XRD, IR, Raman, and elemental analysis. On other hand, the addition of DMF into the reaction solution of dimethylamine and MoO_3 resulted in $((\text{CH}_3)_2\text{NH}_2)_6[\text{Mo}_7\text{O}_{24}]$, while $((\text{CH}_3)_2\text{NH}_2)_2[\text{Mo}_3\text{O}_{10}]$ was obtained by evaporating the reaction solution at 70°C . Solid state heating of the $((\text{CH}_3)_2\text{NH}_2)_6[\text{Mo}_7\text{O}_{24}]$ at 140°C in air produced $((\text{CH}_3)_2\text{NH}_2)_8[\text{Mo}_{10}\text{O}_{34}]$, and heating of the $((\text{CH}_3)_2\text{NH}_2)_2[\text{Mo}_3\text{O}_{10}]$ at 160°C resulted $((\text{CH}_3)_2\text{NH}_2)_4[\text{Mo}_8\text{O}_{26}]$. Ethylammonium monomolybdate, $(\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{MoO}_4$ was prepared by dissolving MoO_3 in an aqueous ethylamine solution and subsequent addition of DMF.

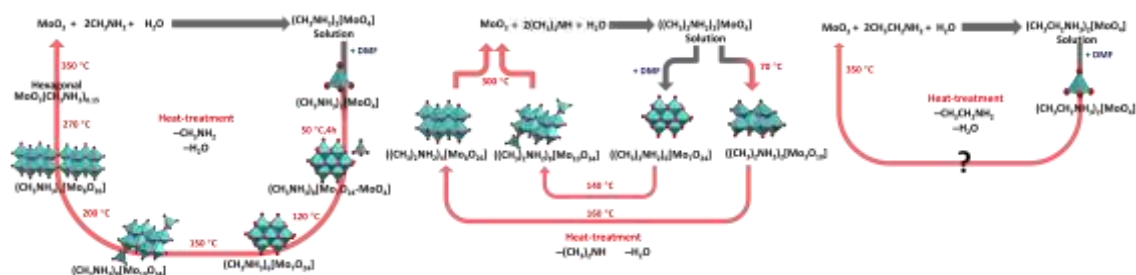


Figure 1. Formation of isopolymolybdates by reaction of MoO_3 , H_2O , and alkylamine and subsequent heating.

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Research keywords: Polyoxometalates, Hydrogen evolution, Heterogeneous system, Photocatalysis, Electrospinning

Polyoxometalates (POMs) embedded photoactive electrospun nanofibers for light-driven hydrogen evolution

In recent years, there has been a growing interest in large-scale heterogeneous light-driven hydrogen evolution systems.^[1] Polyoxometalates (POMs) have been proven to be excellent performers in hydrogen evolution reaction (HER). The integration of hydrogen evolution reaction catalyst (CAT) and molecular photosensitizers (PS) in nanofiber mats is a key factor for the transformation from laboratory-scale particle suspension systems to large-scale industrial application. Nanofibers having larger surface area and tunable morphology are expected to be suitable host for CAT and PS. We demonstrated the fabrication of freestanding electrospun photoactive fibers by integrating HER-CATs and PS during electrospinning into polymeric nanofibers. Initially, we addressed easily accessible components such as POM-CATs ($(n\text{Bu}_4\text{N})_7\text{K}_3[\text{P}_2\text{W}_{18}\text{O}_{62}]$), PS ($[\text{Ru}(\text{bpy})_3]^{2+}$), and polyacrylonitrile (PAN) polymers. The chemical homogeneity of the nanofibers is confirmed by Raman spectroscopy. This system has been used to study the role of material integration, *i.e.*, the role of the local environment of photoactive molecular components, on their light-driven catalytic activity, the excited-state properties of reduced/oxidized states and study electron-transfer between PS and CAT using time-resolved spectroscopic. Furthermore, we integrated PS, CATs, and covalent PS-CAT dyads into polymeric nanofibers to study distance dependencies of light-induced charge-transfer and how inter/intramolecular charge-transfers affect the overall catalytic performance of the functionalized fibers.

References

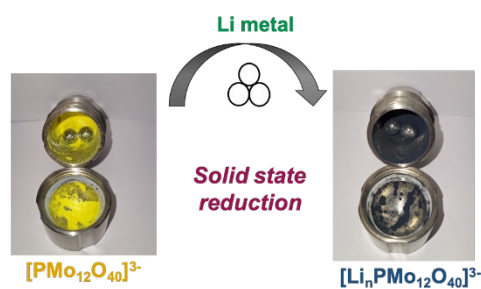
- [1] Z. Wang, C. Li, K. Domen, *Chem. Soc. Rev.* **2019**, *48*, 2109–2125.

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Research keywords: Polyoxometalates, Mechanochemistry, Super-reduction

Mechanochemical Synthesis of Electron-rich Polyoxometalates

The use of mechanical forces to drive chemical reactions, *i.e.* mechanochemistry, has emerged during the last decade due to its potential to establish green and sustainable synthetic methods.[1] In this talk, I will present the first systematic investigation of mechanochemical reduction of these promising charge storage and energy conversion materials, demonstrating solvent-free access to super-reduced POMs and revealing some of the complex, unexplored chemistry of these electron-rich molecular metal oxides. The Keggin-type phosphomolybdate $(\text{TBA})_3[\text{PMo}_{12}\text{O}_{40}]$ was reacted with n equivalents of lithium metal ($n = 1 - 24$) to generate a series of electron-rich $\text{Li}_n\text{Mo}_{12}$ species. FTIR analysis of solid $\text{Li}_n\text{Mo}_{12}$ products revealed the lengthening/weakening of terminal $\text{Mo}=\text{O}$ bonds with increasing levels of reduction, while EXAFS spectra indicated the onset of $\text{Mo}-\text{Mo}$ bond formation at $n \sim 8$ and a significant structural change at $n > 12$. Successive Mo^{VI} reductions were also monitored by XANES and XPS and, at $n = 24$, results were consistent with the formation of one $\text{Mo}^{\text{IV}}-\text{Mo}^{\text{IV}}$ bonded $\{\text{Mo}^{\text{IV}}_3\}$ triad together with Mo^{V} sites, rather than four $\{\text{Mo}^{\text{IV}}_3\}$ triads in the polyoxometalate framework. Broad resonances in ^{31}P NMR spectra of propylene carbonate solutions of $\text{Li}_n\text{Mo}_{12}$ when $n \geq 16$ most likely arise from aggregation through $\text{Li}-\text{O}$ bonds that are formed even in $\text{Li}_2\text{Mo}_{12}$, which crystallised from MeCN to give $(\text{TBA})_4[\text{PMo}_{12}\text{O}_{40}\{\text{Li}(\text{NCMe})\}]$, where $\{\text{Li}(\text{NCMe})\}^+$ is bonded to four oxygens of a tetragonal site on the Keggin anion. In this regard, the use of mechanochemistry in the reduction of POMs represents a new approach in the search for a better fundamental understanding of the electronic properties and reactivity of electron-rich nanoscale metal oxides. These findings are relevant for applications that use the massive electron storage capabilities of POMs. [2]



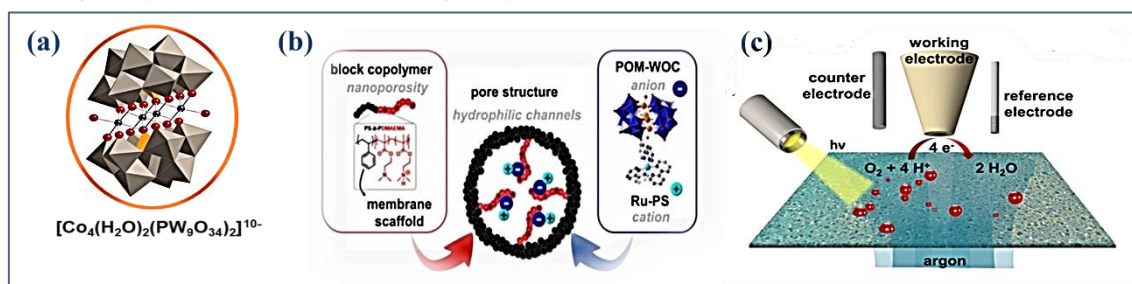
[1] James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Frišćić, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; *et al.* Chem. Soc. Rev. **2012**, 41, 413. [2] Magda Pascual-Borras, Elisabetta Arca, Hirofumi Yoshikawa, Thomas Penfold, Paul G. Waddell and R. John Errington, *Submitted*, **2023**.

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Research keywords: polyoxometalates, porous block copolymer, photocatalysis, O₂ evolution


POMbranes: A soft matter matrix for light driven water oxidation catalysis

Light driven catalytic water splitting to produce solar hydrogen/oxygen is more relevant and topical than ever. Polyoxometalates (POMs) are promising candidates for water oxidation or proton reduction which are extensively studied [1]. Here, we report a photocatalytic soft matter system that consists of a block copolymer membrane functionalized with a polyoxometalate based water oxidation catalyst (POM-WOC) and a molecular photosensitizer (PS). These so called, “POMbranes” are stabilized by electrostatic/supramolecular or covalent interactions and form active hybrid materials for the light driven water oxidation [2]. For the measurements, scanning electrochemical microscopy (SECM) is used to measure light induced O₂ evolution with high spatial and temporal resolution; micro-X-ray fluorescence (μ -XRF) is used to study local distribution of molecular components. A thorough characterizations revealed that the variations in O₂ evolution is attributed to the membrane structure heterogeneity and therefore, the heterogeneity in POM-WOC/PS distribution.



Reference

- [1] Gao, D., Trentin, I., Schwiedrzik, L., Gonzalez, L., Streb C., *Molecules* **2020**, 25, 157.
- [2] Kund J., Kruse J.-H., Gruber A., Trentin I., Langer M., Read C., Neusser G., Blaimer D., Rupp U., Streb C., Leopold K., Schacher F. H., Kranz C., *Angew. Chem. Int. Ed.* **2023**, 62, e202217196.

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Research keywords: polyoxometalates, ionic liquids, water purification, membrane reactors.

Develop of POM-ILs for membrane reactor structure functionalization

Human activities negatively impact the environment in several different ways leading to environmental degradation and loss of resource bases. Plastic pollution is an emerging worldwide concern and constitutes a serious environmental threat to our planet, with impacts on ecological systems and public health becoming gradually apparent. Plastics have recently been detected in human blood and stool [1], and microplastics are detected in all environmental compartments including water, soil, and air. To reduce plastic pollution, there is a concurrent interest in the development and optimization of an alternative and promising method for microplastic degradation from wastewater streams. In this regard, considerable attention was paid to the use of so-called polyoxometalate-ionic liquids (POM-ILs). Polyoxometalates (POMs) are a class of inorganic compounds that consist of metal oxo clusters. These clusters can exhibit diverse structures and have a variety of applications. When combined with ionic liquids (ILs), which are organic salts in a liquid state at or near room temperature, they can form polyoxometalate-ionic liquid hybrids (POM-ILs) with unique properties. This combination has shown promise in various applications, including water treatment. Recently, POM-IL already showed high removal efficiency of multiple organic and inorganic pollutants under flow [2]. This study proposes the development of novel POM-IL-enzyme hybrid materials as mobile attachment sites to link enzymes to porous solid oxide surface for membrane reactor structure functionalization. Therefore, lacunary Keggin POMs will be electrostatically conjugated with organic quaternary ammoniums or phosphonium cations that provide the membranes with plastic adsorption capacities and anti-biofouling properties, as well as with enzymes that degrade the absorbed plastics.

Reference.

- [1] Leslie, Heather A., Martin Jm Van Velzen, Sicco H. Brandsma, A. Dick Vethaak, Juan J. Garcia-Vallejo, and Marja H. Lamoree. "Discovery and quantification of plastic particle pollution in human blood." *Environment international* 163 (2022): 107199.
- [2] Oseghe, Ekemena O., Fabian Guba, Archismita Misra, Ruihao Gong, Rongji Liu, Siegfried R. Waldvogel, Dirk Ziegenbalg, Carsten Streb, and Dandan Gao. "A scalable flow device for the removal of organic and inorganic pollutants from water." *Device* 1, no. 2 (2023).

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Research keywords: polyoxometalates, photocatalysis, organic-inorganic hybrids, ARC chemistry, single electron transfer (SET)

Organofunctionalised Borotungstate Polyoxometalates as Photocatalysts for the Oxidative Cross-Coupling of Amines

Polyoxometalates (POMs) have found utility facilitating various organic transformations, including oxidations and reductions, hydrolysis and Lewis acid processes, acting as both electrocatalysts¹ and photocatalysts.² However, despite research efforts, the decatungstate anion remains the only POM with competitive photoactivity in oxidative HAT chemistry of organic substrates.

The organofunctionalisation of POMs represents a powerful tool for modular installation of organic and organometallic moieties onto polyoxometalates. This design flexibility has led to elegant cooperative photocatalytic systems where POMs are coupled to photosensitizers or catalytic centers to achieve photoredox of small molecules.^{3,4} Recently, we have demonstrated that organofunctionalisation can also be used to increase the photocatalytic activity of POM clusters through modulation of the bridging atom and electronic properties of simple aryl tethers.^{5,6}

In this work, we combine the above findings with considerations of cluster charge and central templating atom effects to design a series of phenyl functionalized borotungstate hybrids bearing different bridging atoms. Cyclic voltammetry demonstrates that organofunctionalization with different bridging atoms effectively modulates the LUMO of the POM compared to the plenary structure. We show that the phenyl phosphonate borotungstate hybrid is an effective photocatalyst for the oxidative coupling of a range of benzyl amines at room temperature – highlighting the untapped potential of simple hybrid polyoxometalates as photocatalysts for organic transformations.

Reference,

1. I. L. Zhang, S. Li, C. J. Gómez-García, H. Ma, C. Zhang, H. Pang and B. Li, *ACS Appl Mater Interfaces*, **2018**, *10*, 31498–31504.
2. D. Ravelli, M. Fagnoni, T. Fukuyama, T. Nishikawa and I. Ryu, *ACS Catal.*, **2018**, *8*, 701–713.
3. Y. Luo, S. Maloul, S. Schönweiz, M. Wächter, C. Streb and B. Dietzek, *Chem.-Eur.J.*, **2020**, *26*, 8045-8052.
4. M. Lu, M. Zhang, J. Liu, T. Y. Yu, J. N. Chang, I. J. Shang, S. L. Li and Y. Q. Lan, *JACS*, **2022**, *144*, 1861-1871
5. S. Fujimoto, J. M. Cameron, R. J. Wei, K. Kastner, D. Robinson, V. Sans, G. N. Newton and H. Oshio, *Inorg. Chem.*, **2017**, *56*, 12169-12177.
6. A. J. Kibler, N. Tsang, M. Winslow, S. P. Argent, H. W. Lam, D. Robinson and G. N. Newton, *Inorg. Chem.*, **2023**, *62*, 3585-3591.

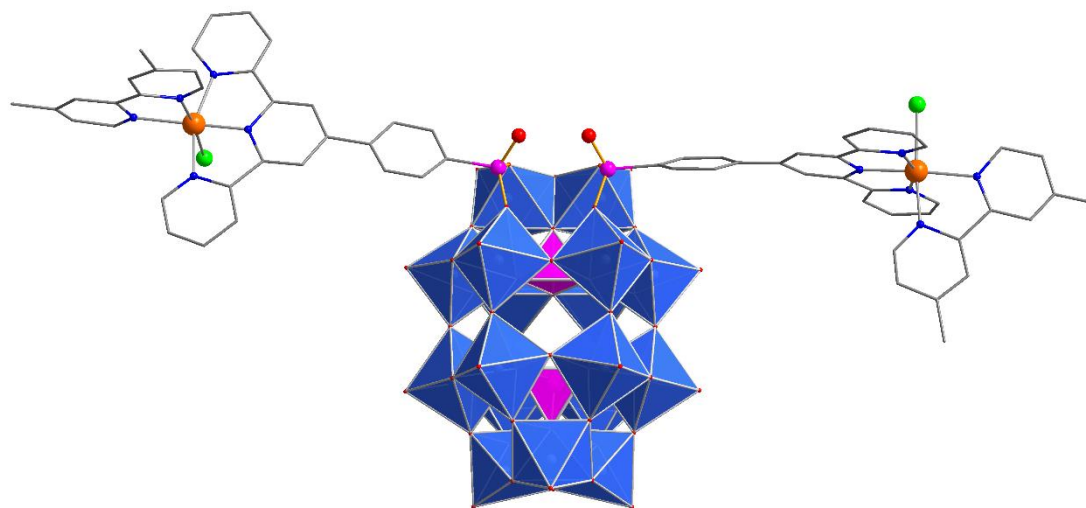
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Research keywords: Polyoxometalates, Catalysis, Organic-Inorganic Hybrid Materials

Hybrid Organic-Inorganic Polyoxometalates: A Perspective in Design

Polyoxometalates (POMs) are polyanionic molecular metal oxide clusters with diverse structures and properties that have a capacity for reversible multi-electron redox chemistry. Further modification to include organic moieties permits the design and synthesis of organic–inorganic hybrid systems that demonstrate synergistic properties leading to applications in controlled self-assembly, energy storage, and catalysis amongst others. By tailoring the nature of the organic unit in particular, the resulting hybrid species can be finely tuned to impact these functions.

A perspective in the current design strategies and future directions will be presented.^{1,2} A multi-component coordination compound, in which ruthenium antenna complexes are connected to a POM core will also be discussed.¹ This hybrid cluster selectively promotes the electrochemical conversion of CO₂ to C1 feedstocks, a unique cooperative effect, which cannot be replicated in the absence of direct hybridisation of the catalytic and polyoxoanion components into a single active complex.



Reference.

- [1] Newton, G. N., *et al.*, *Chem. Commun.*, **2023**, 59, 10801-10804.
- [2] Newton, G. N., *et al.*, *Angew. Chem. Int. Ed.* **2023**, 62, e202302446.

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Research keywords: Hybrid Organic-Inorganic Polyoxometalates, Redox chemistry, Micelles, Nanotubes, Transmission Electron Microscopy, Impedance Data, Nanogaps and Memristors.

**Self-assembly of hybrid inorganic-organic polyoxometalate amphiphiles:
interconversion between 0D micelles and 3D extended assemblies.**

Controlled aggregation of functional molecules, both in solution and in the solid state, allows the preparation of nanomaterials with desirable structure, dimension, and composition.¹ The self-assembly mechanism of the POM $\{W_{17}C_n\}$, a type II hybrid inorganic-organic polyoxometalate amphiphile, allows dynamic interconversion from 0D spherical micelles to highly ordered cylindrical micelles in solution.² Here we investigate the impact of different parameters on the kinetics of the self-assembly process. We have previously shown that the chain length of the hydrophobic groups impacts micelle size and stability,³ and now demonstrate the role played by micelle concentration on the assembly and consequently the conductivity in solution. Focusing on the 1.4 mM POM $\{W_{17}C_{20}\}$ solution we observed interconversion from micelles to nanotubes over time. Moreover, deposition of aliquots on lasey carbon and HOPG has shown aggregation behavior dependent on weak interactions with the respective substrates.⁴ Finally, we show that freeze-drying the 1.4 mM POM micelle solution produces a sponge-like 3D mesh of cylindrical micelles. Preliminary tests suggest that the sponge-like material pressed into pellets can find applications in memristors for non-volatile memory storage applications.

Reference.

- [1] E. Hampson, J. M. Cameron, S. Amin, J. Kyo, J. A. Watts, H. Oshio, and G. N. Newton; *Angew. Chem.*, **2019**, 131, 18449-18453.
- [2] K. Kastner, A. J. Kibler, E. Karjalainen, J. A. Fernandes, V. Sans and G. N. Newton; *J. Mater. Chem. A*, **2017**, 5, 11577-11581.
- [3] S. Amin, J. M. Cameron, J. A. Watts, D. A. Walsh, V. Sans and G. N. Newton; *Mol. Syst. Des. Eng.*, **2019**, 4, 995.
- [4] S. Amin, J. M. Cameron, R. B. Cousins, J. Wrigley, L. Liirò-Peluso, V. Sans, D. A. Walsh and G. N. Newton; *Inorg. Chem. Front.*, **2022**, 9, 1777.

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Research keywords: POMs, nanotubes, photochemistry, host-guest, charge-transfer

HOST–GUEST CHEMISTRY IN BORON NITRIDE NANOTUBES: INTERACTIONS WITH POLYOXOMETALATES

Boron nitride nanotubes (BNNTs) are an emerging class of molecular container offering new functionalities and possibilities for studying molecules at the nanoscale.¹ Herein, BNNTs are demonstrated as highly effective nanocontainers for polyoxometalate (POM) molecules.² The encapsulation of POMs within BNNTs occurs spontaneously at room temperature from an aqueous solution, leading to the self-assembly of a POM@BNNT host–guest system. Analysis of the interactions between the host-nanotube and guest-molecule indicate that there are interactions between W=O groups of the POM and boron atoms of the BNNT lattice. The transparent nature of the BNNT nanocontainer allows extensive investigation of the guest-molecules by photoluminescence, Raman, UV–vis absorption, and EPR spectroscopies. These studies reveal considerable energy and electron transfer processes between BNNTs and POMs, likely mediated *via* defect energy states of the BNNTs. Furthermore, these processes result in the quenching of BNNT photoluminescence at room temperature, the emergence of new photoluminescence emissions at cryogenic temperatures (<100 K), a photochromic response, and paramagnetic signals from guest POMs. These phenomena offer a fresh perspective on host–guest interactions within nanotubes and open pathways for harvesting the functional properties of these hybrid systems.

- (1) Walker, K. E.; Rance, G. A.; Pekker, Á.; Tóháti, H. M.; Fay, M. W.; Lodge, R. W.; Stoppiello, C. T.; Kamarás, K.; Khlobystov, A. N. Growth of Carbon Nanotubes inside Boron Nitride Nanotubes by Coalescence of Fullerenes: Toward the World’s Smallest Coaxial Cable. *Small Methods* **2017**, *1* (9), 1700184.
- (2) Jordan, J. W.; Chernov, A. I.; Rance, G. A.; Stephen Davies, E.; Lanterna, A. E.; Alves Fernandes, J.; Grüneis, A.; Ramasse, Q.; Newton, G. N.; Khlobystov, A. N. Host–Guest Chemistry in Boron Nitride Nanotubes: Interactions with Polyoxometalates and Mechanism of Encapsulation. *J. Am. Chem. Soc.* **2023**, *145* (2), 1206–1215.

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Research keywords: Electrocatalysis, oxygen evolution reaction, nanoscale, core-shell

Electrochemical oxygen evolution reaction catalysed by metal oxides through a single layer of carbon


The availability of efficient electrocatalysts is key to the development of next-generation electrolyzers for water splitting to produce so-called ‘green hydrogen’ for a future hydrogen economy.¹ The kinetically sluggish oxygen evolution reaction (OER), one half of the overall water splitting reaction, acts as the bottle-neck to efficient water electrolysis. Designing cheap, heavy-metal-free OER electrocatalysts that deliver both high activity and stability remains the largest obstacle for delivering sustainable hydrogen. A common method to increase the stability of OER catalysts while keeping metal content low is the use of carbon-coated metal/metal oxide (nano)particles. However, the role these carbon coatings play in electrocatalysis in these systems is still poorly understood.^{2,3} We found that the carbon coating itself acts as the active site in OER, with the underlying material activating the carbon through a charge transfer mechanism. This was demonstrated by encapsulating metal oxides within single-walled carbon nanotubes, giving nanoparticles with diameters of < 2 nm coated in a single layer of carbon, which showed an increase in both activity and stability compared to pristine carbon nanotubes. Access to the encapsulated metal oxides was blocked by plugging the nanotubes with fullerenes, shutting off metal oxide redox processes without affecting catalytic activity, showing that the carbon surface was the active site. In-situ spectroelectrochemical Raman demonstrated a degree of charge transfer from the carbon to the metal oxide during OER, which was corroborated through computational methods. This charge transfer results in a decrease in electron density on the carbon surface, allowing for more facile binding of $\cdot\text{OH}$, the first step of OER, which is key to the increase in activity. This understanding of how carbon coatings play an active role in electrocatalytic reactions is crucial for further electrocatalyst development, with the proposed charge transfer driven mechanism tunable to both oxidative and reductive reactions.

Reference.

[1] Majumdar, A., Deutch, J. M., Prasher, R. S. & Griffin, T. P. A framework for a hydrogen economy. *Joule* **5**, 1905–1908 (2021).

[2] Deng, J., Deng, D. & Bao, X. Robust Catalysis on 2D Materials Encapsulating Metals: Concept, Application, and Perspective. *Advanced Materials* **29**, 1606967 (2017)

[3] Melchionna, M., Fornasiero, P. & Prato, M. Into the carbon: A matter of core and shell in advanced electrocatalysis. *APL Materials* **8**, 020905 (2020)

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Research keywords: polyoxometalate, Keplerate, redox-active, adsorption.

Redox-active Keplerates Capsule Encapsulated with Keggin-Type POM for Cesium Ion Uptake

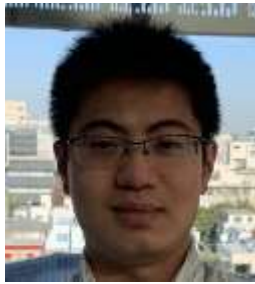
The uptake of cations has always been an important topic in materials chemistry, and polyoxometalates (POMs) have long been studied as cation exchangers for the removal of toxic metal ions.^[1, 2] At present, POM-based compounds for cation-uptake can be divided into three types: (1) cation exchange with POM-based ionic solids,^[2] (2) cation trapping by POM molecules with inorganic crown ethers or cryptands,^[3, 4] (3) cation absorption induced by redox reactions introduced to POM compounds.^[5] However, there are few reports on cation uptake by the utilization of redox reaction.

Considering that reduction-induced cation exchange is a property unique to redox active POM-based compounds, we previously reported a charge-neutral Keplerate, initially described by Müller and his co-workers.^[6] This structure contains 20 crown-ether-like pores and results in exciting performance of Cs⁺ selectively uptake through a cation-coupled electron-transfer (CCET) reaction.^[7] During the whole adsorption process, Cs⁺ ions were selectively trapped into both Keggin-type POM and crown-ether-like pores via cation-coupled electron-transfer reaction, which is not only the denticity and coordination ability of POM are utilized, but also the redox property of POM contributes, showing an unique and excellent Cs⁺ uptake effect.

In this project, we selected three Keplerate capsules that are structurally similar but have different compositions of metallic elements. In the process of cation absorption via CCET reaction, three materials exhibited distinct adsorption properties, which is helpful for us to further understand the mechanism of Keplerate's absorption of Cs⁺ via CCET reaction and provide new references for solution of environmental problems.

Reference.

- [1] A. Tripathi, D. G. Medvedev, J. Delgado and A. Clearfield, *J. Solid State Chem.*, 2004, 177, 2903–2915.
- [2] V. Pekarek and V. Vesely, *Talanta*, 1972, 19, 1245–1283.
- [3] K. Fukaya and T. Yamase, *Angew. Chem., Int. Ed.*, 2003, 42, 654–658.
- [4] A. Yoshida, Y. Nakagawa, K. Uehara, S. Hikichi, and N. Mizuno, *Angew. Chem., Int. Ed.*, 2009, 48, 7055–7058.
- [5] S. Uchida, *Chem. Sci.*, 2019, 10, 7670–7679.
- [6] A. Müller, S. K. Das, H. Bögge, M. Schmidtman, A. Botar and A. Patrut, *Chem. Commun.*, 2001, 657–658.
- [7] Tamai N, Ogiwara N, Hayashi E, Kamata K, Misawa T, Ito T, Kojima T, Segado M, Petrus E, Bo C, Uchida S, *Chem Sci.*, 2023, 14, 5453-5459.

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Research keywords: Electrochemical CO₂ Reduction, Electrode catalysts

Electrochemical CO₂ Reduction using Polyoxometalate-Modified Electrodes


Production of valuable carbon resources by electrochemical CO₂ reduction reaction (CO₂RR) is one of the promising solutions for addressing both global warming and depletion of fossil fuels, and therefore, CO₂RR has attracted much attention from both industry and academia^{[1][2]}. In the field of CO₂RR, there is a considerable demand for the development of electrocatalysts that exhibit both high selectivity and high durability. Various materials have been explored as CO₂RR catalysts. In our laboratory, we have developed synthetic methods for various metal-introduced polyoxometalates (POMs) possessing multinuclear metal sites. Importantly, even if the structural changes occur in POMs during the reaction, *in situ* formed catalytically active sites are protected by surrounding MO_x species (M = W, Mo, V, etc.), preventing the deactivation of catalysts. Therefore, these advantages make POMs attractive for CO₂RR catalysts.

In this study, we aimed to develop robust CO₂RR catalysts that can selectively produce specific product by creating stable active sites using POM-modified electrodes. To achieve this, metal-introduced POMs were immobilized on carbon supports (C) to create POM-carbon composites (POM/C). Subsequently, POM/C were deposited on carbon electrodes, and the catalytic performance for CO₂RR was evaluated. We also investigated electrodes and catholyte after reaction by various characterization methods.

Reference.

[1] P. Shao, W. Zhou, Q.-L. Hong, L. Yi, L. Zheng, W. Wang, H.-X. Zhang, H. Zhang, J. Zhang, *Angew. Chem. Int. Ed.* **2021**, *60*, 16687.

[2] H. Tabassum, X. Yang, R. Zou, G. Wu, *Chem Catal.* **2022**, *2*, 1561.

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Research keywords: peroxopolyoxometalate, rare earth element, diphosphate, porous crystal

Synthesis of a cyclic peroxopolytungstate containing diphosphates and rare earth elements and its porous crystal

【Introduction】 Polyoxometalates (POMs) have high structural diversity, and their chemical and physical properties can be controlled by their structures and compositions. POMs with a coordinated peroxy group are called peroxy-POMs. In peroxy-POMs, the coordination sphere changes from octahedral to decahedral, forming structures different from ordinary POMs.

As a part of peroxy-POMs research, peroxopolytungstates containing diphosphate and rare earth elements have been investigated.

【Result and Discussion】 A novel peroxy-POM [$\{\text{RE}(\text{OH}_2)_4(\text{P}_2\text{O}_7)\text{W}_6\text{O}_{15}(\text{O}_2)_4\}_6]^{18-}$

(RE6P12W36 : RE = La, Ce, Pr, Nd, Sm, Eu : Figure.1)

has been synthesized as Me_4N^+ and Et_4N^+ salts. The POM forms a cyclic structure with an inner diameter of 16 Å by bridging six hexanuclear tungstate units with diphosphates and rare earths. In the crystal, RE6P12W36 are aligned along the *c*-axis to form a porous crystal with 1D channels (Figure. 2), which are filled with crystalline water and counter cations. Water sorption isotherms and proton conductivity studies are currently underway, and the results will be presented at the conference.

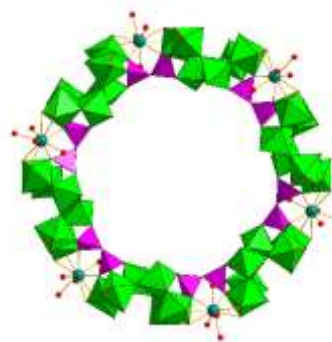


Figure. 1 Anion structure of RE6P12W36

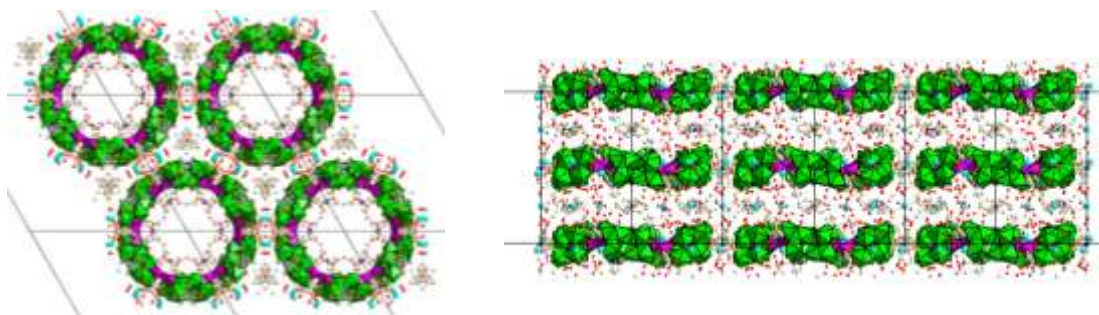



Figure. 2 Crystal structure of RE6P12W36 - Et_4N^+ salt.

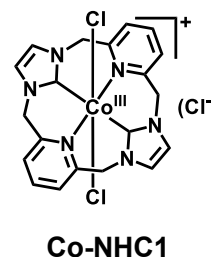
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Research keywords: Hydrogen Evolution; Cobalt complex; Electrochemistry; Turnover Frequency (TOF); N-Heterocyclic Carbene (NHC)

Precise Turnover Frequency Estimation in Electrochemical Hydrogen Evolution from Water Catalyzed by a Co-NHC Complex

Hydrogen production based on solar water splitting has attracted great attention for the realization of sustainable energy society. Our laboratory previously reported that an N-heterocyclic carbene cobalt complex, **Co-NHC1**, promotes photochemical hydrogen evolution from water with low driving force.^[1,2] In this study, the advanced electrochemical analyses were conducted to elucidate the mechanism of hydrogen evolution reaction (HER) catalyzed by **Co-NHC1**.


In linear sweep voltammogram (LSV) measurement under the condition of pH 7 aqueous phosphate buffer, a large catalytic current with the onset potential of -1.1 (V vs. SCE) was observed in a cathodic sweep. In this pH 7 conditions, the concentration dependence of the phosphate buffer solution was evaluated through LSV. As a result, it was found that one H_2PO_4^- molecule is involved as a proton mediator during the PCET-based (proton-coupled electron transfer) reduction process towards Co(II), which is considered as the rate-limiting step. Interestingly, a linear correlation was observed between the maximum catalytic current ($i_{\text{cat,max}}$) and the concentration of **Co-NHC1**, where $i_{\text{cat,max}}$ values were determined from the plateau-shaped currents obtained by increasing the scan rate. Therefore, it can be concluded that the HER catalyzed by **Co-NHC1** proceeds via a unimolecular pathway.



It was found that the catalyst is coated over the surface of the electrode just by dipping the glassy carbon electrode to the catalyst solution. The LSV measurement in the blank phosphate buffer solution using the electrode dipped in the Co-NHC solution resulted in the minor increase of current compared to the blank measurement. This effect was eliminated to calculate turnover frequency (TOF) of HER catalyzed by **Co-NHC1** under the homogeneous conditions. The TOF was estimated to be 22,000,000 s^{-1} , showing that **Co-NHC1** has exceptionally high catalytic activity of HER.

[1] K. Kawano, K. Yamauchi, and K. Sakai, *Chem. Commun.* **50**, 9872-9875 (2014).

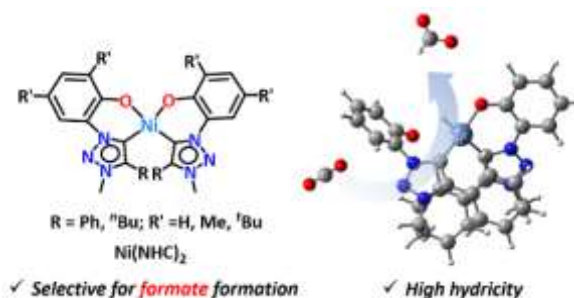
[2] K. Yatsuzuka, K. Yamauchi, K. Kawano, H. Ozawa, and K. Sakai, *Sustainable Energy Fuels* **5**, 740-749 (2021).

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Research keywords: CO₂ Reduction; Hydride; Formate; DFT Calculations.

The Mechanism of Ni-NHC CO₂ Reduction Catalysis Predominantly Affording Formate via a Metal Hydride Intermediate


Formic acid/formate (HCOOH/HCOO⁻) formation reaction through the reduction of CO₂ is of great interest due to its potential to convert a greenhouse gas into valuable products for synthesis, hydrogen storage, and other industrial applications. However, various earth-abundant-metal based catalysts often produce carbon monoxide (CO) as major product of CO₂ reduction instead of formic acid. We focus on nickel based NHC complexes known for their selectivity in formate formation, which were reported by Albrecht and colleagues.¹ Since the underlying mechanism has not been observed, our study aims to elucidate the mechanism of CO₂ reduction to HCOO⁻ using density functional theory (DFT) calculations. Specifically, we focus on investigating the mechanism of catalysis by Ni(NHC)₂.



Through extensive DFT calculations, the energy states, geometries, and activation barriers of potential intermediates have been analyzed. Our research challenges the previously suggested Ni(III)-hydride mechanism, proposing instead that Ni(II)-hydride is the key intermediate in CO₂ reduction to formate. The findings reveal that the Ni(II)-hydride intermediate, formed through a proton-coupled electron transfer (PCET) process, presents a more energetically favorable pathway compared to the Ni(III)-hydride. Besides, the Ni(II)-hydride exhibits significant hydricity, enabling effective hydride transfer to the carbon center of CO₂.² This mechanism bypasses the high-energy state and kinetic challenges associated with the Ni(III)-hydride pathway, leading to a more direct and efficient formation of formate.

Reference

- 1 S. Bertini, M. Rahaman, A. Dutta, P. Schollhammer, A. V. Rudnev, F. Gloaguen, P. Broekmann and M. Albrecht, *Green Chem.*, 2021, **23**, 3365–3373.
- 2 K. M. Waldie, A. L. Ostericher, M. H. Reineke, A. F. Sasayama and C. P. Kubiak, *ACS Catal.*, 2018, **8**, 1313–1324.

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Research keywords: Polyoxometalate, Silver Cluster, Porous Ionic Crystals

Size-Controlled Synthesis of Small Silver Clusters in Porous Ionic Crystals based on Dawson-type Polyoxometalate

Ag clusters consisting of about ten or less atoms (few-atom Ag clusters) are known to show unique electronic, optical, or catalytic properties, which are not observed in the corresponding bulk samples.^[1] However, since small Ag clusters have a strong tendency to aggregate, size-controlled synthesis is still challenging and has been recognized as an important issue both in basic and applied sciences.


In recent years, anionic metal-oxygen clusters called polyoxometalates (POMs) have been utilized in combination with molecular cations as building blocks to synthesize porous ionic crystals (PICs). A noteworthy feature of PICs is their redox-activity, i.e., PICs can store/release electrons in cooperation with incorporation/release of cations to compensate for charge changes. We have recently shown that redox-active PICs comprising a Dawson-type POM $[P_2W^{VI}_{18}O_{62}]^{6-}$ serve as scaffolds to synthesize Ag clusters by utilizing their reducibility and porosity. Specifically, the electrons stored in the reduced POMs are transferred to Ag^+ followed by aggregation of Ag^0 and Ag^+ , the Ag clusters are stabilized in the pores as counter cations of POMs, and the small pores inhibit further growth of the Ag clusters.^[2]

In this work, we employed isostructural redox-active PICs $A_3[Cr_3O(OOCH)_6(ety)_3]_3[P_2M^{VI}_{18}O_{62}] \cdot nH_2O$ (ety = 4-ethylpyridine; A = K or NH_4 ; M = Mo or W) as scaffolds for size-controlled synthesis of few-atom Ag clusters.^[3] The versatile choice of components enables to control essential parameters such as reducing power and ion-exchange ability without altering the crystal structure. Ag clusters with three ($[Ag_3]^+$), four ($[Ag_4]^{2+}$), or six ($[Ag_6]^{2+}$) Ag atoms, emitting blue, green, or red colors, respectively, are formed and stabilized in PICs. We found that the size of Ag clusters can be controlled by i) the time for reducing the PICs and ii) the types of constituent ions or elements, which is related to the redox activity and ion exchange rate of the PICs. The cluster size correlates with the amounts of electrons transferred from the PIC scaffold to Ag^+ , characterized by the combination of photoluminescence (PL) spectra, X-ray photoelectron spectroscopy (XPS), and X-ray absorption fine structure (XAFS). These results demonstrate a rational method for size-controlled synthesis of ligand-free and air-stable few-atom Ag clusters in crystalline porous solids.

[1] K. Yonesato, K. Yamaguchi, K. Suzuki, *et al.*, *Nat. Chem.*, **2023**, *15*, 940.

[2] N. Haraguchi, N. Ogiwara, S. Uchida, *et al.*, *Eur. J. Inorg. Chem.*, **2021**, *2021*, 1531.

[3] N. Haraguchi, N. Ogiwara, S. Uchida, *et al.*, *Small*, **2023**, *19*, 2300743.

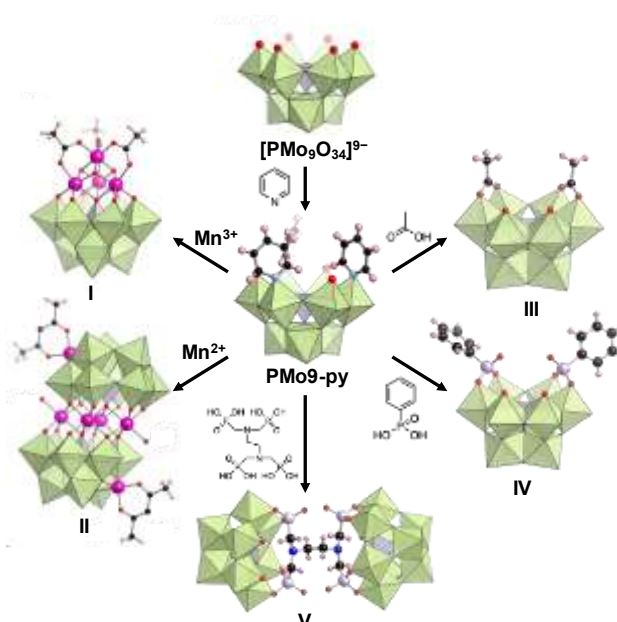
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Research keywords: Polyoxometalates, Lacunary Polyoxomolybdates

A Protecting Group Strategy to Access Stable Lacunary Polyoxomolybdates for Synthesizing Molecular Hybrids


Lacunary polyoxometalates (POMs) are one of the important inorganic molecules for constructing molecular hybrids in which the interaction of POMs with organic ligands or metal ions produces synergistic effects. Lacunary polyoxomolybdates are attractive POMs because of their unique electrochemical and photochemical properties, however, their low stability has made it difficult to synthesize and use such hybrids. We have recently reported that coordination of monodentate pyridine molecules can stabilize lacunary polyoxomolybdates ($[\text{PMo}_9\text{O}_{34}]^{9-}$).^[1] In this study, we present a “protecting group strategy” synthesis of two types of tetranuclear manganese clusters (**I**, **II**)^[2] and three types of POM–organic hybrids (**III–V**)^[3] using the pyridine-protected A- α -Keggin-type trivacant lacunary polyoxomolybdate **PMo9-py** as a precursor.

By reacting **PMo9-py** with manganese species in organic solvents, two types of tetranuclear manganese clusters, a cubane-type structure (**I**) and a planar-type structure (**II**), were selectively synthesized. In the same way, by reacting **PMo9-py** with multidentate carboxylate and phosphonate ligands with a single reactive site, monomeric structures with two ligands introduced **III** and **IV** were synthesized, respectively. Furthermore, by using phosphonate ligands possessing multiple reactive sites, dimeric structure **V** was synthesized.



References.

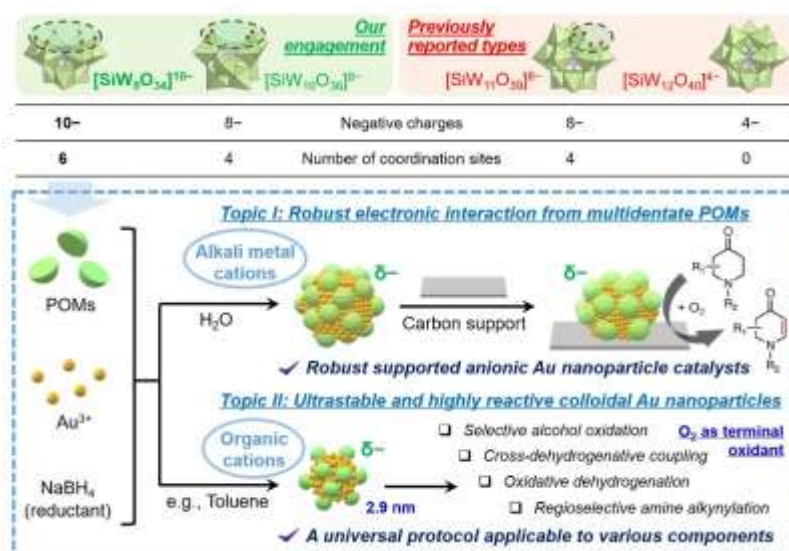
[1] Li, C.; Mizuno, N.; Yamaguchi, K.; Suzuki, K. *J. Am. Chem. Soc.* **2019**, *141*, 7687. [2] Li, C.; Jimbo, A.; Yamaguchi, K.; Suzuki, K. *Chem. Sci.* **2021**, *12*, 1240. [3] Jimbo, A.; Li, C.; Yonesato, K.; Ushiyama, T.; Yamaguchi, K.; Suzuki, K. *Chem. Sci.* **2023**, *14*, 10280.

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Research keywords: polyoxometalates, gold nanoparticles, metal nanoparticles, catalyst design


Catalyst Design of Metal Nanoparticle-Based Materials Using Multidentate Polyoxometalate Modification

Metal nanoparticles are fascinating materials, the hybrids of which with polyoxometalates (POMs) have recently attracted much attention in diverse fields.¹ Herein, based on our previous engagement on developing metal(-oxo) nanoclusters using multidentate POMs, we utilized multidentate POMs in modifying metal nanoparticles for the first time, and elucidated the existence of robust electronic interaction from multidentate POMs to gold nanoparticles even after being immobilized on carbon support.² We confirmed that electronic states of carbon-supported anionic gold nanoparticles can be sequentially modulated, leading to activity-control and much enhanced stability comparing to commercial Au/C catalyst in oxidative dehydrogenation of piperidone derivatives. Furthermore, by utilizing the structural stability of multidentate POMs in nonpolar solvent systems, ultrastable and highly reactive colloidal gold nanoparticles were successfully prepared.³ According to a series of experimental results, characterization and theoretical calculation findings, those small gold nanoparticles were found to maintain their particle size under practical conditions of high metal concentration, long-term storage, heating, and base addition, and show excellent catalytic properties in various types of oxidation reactions by using oxygen as the terminal oxidant.



Reference.

[1] K. Xia, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214506. [2] K. Xia, T. Yatabe, K. Yonesato, T. Yabe, S. Kikkawa, S. Yamazoe, A. Nakata, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205873. [3] K. Xia, *et al.* manuscript under review (second-round).

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Synthesis and Catalytic Property of Nitrate-Incorporated Octadecavanadates

Vanadium-oxygen cluster anions, called polyoxovanadates, exhibit structural versatility. By the spherical condensation of VO₅ square pyramids directing their square base to the center of the sphere, the inside of the sphere exhibits the unique electrostatic field which act as an anion stabilizer.^[1] Although some polyoxovanadates show the catalytic properties for the several oxidation reactions, it is difficult to determine the accurate active vanadium sites. The local structure control among the related polyoxovanadates leads to understand the reactivity of the specific sites.

Octadecavanadonitrate (**V18**) is composed of two V⁴⁺ and sixteen V⁵⁺ as the shell and one nitrate at the center.^[2] The shape of **V18** is ellipsoid and the top and bottom parts of the ellipsoid (cap parts) are the square pyramidal V⁴⁺ units. **V18** showed reversible redox property. In this work, one-electron-oxidized species of **V18** (**V18ox**) was isolated. From the x-ray crystallographic analysis, the structure of **V18ox** was retained compared to that of **V18**. The V–O bond lengths of one of the cap parts are shorter than those of the original **V18**, showing that the one of the cap part is oxidized to V⁵⁺. Compound **V18** and **V18ox** was acted as the efficient catalyst for the selective oxidation of sulfide with *tert*-butyl hydroperoxide (Fig. 1). By the comparison among the derivatives of **V18**, the possible active site was proposed.

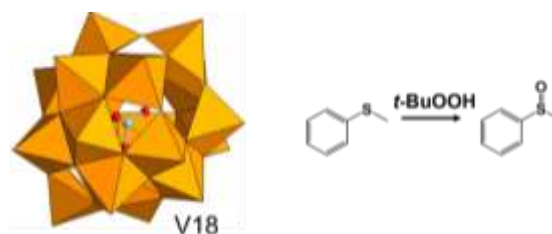



Fig. 1 Structure of nitrate-incorporated octadecavanadate and thioanisole reaction

[1] (a) Y. Kikukawa, H. Kitajima, S. Kuwajima, Y. Hayashi, *Molecules*, **2020**, *25*, 5670. (b) S. Kuwajima, Y. Kikukawa, Y. Hayashi, *Chem. Asian J.* **2017**, *12*, 1909.

[2] (a) Y. Koyama, Y. Hayashi, K. Isobe, *Chem. Lett.* **2008**, *37*, 578. (b) S. Greiner, J. Hettig, A. Laws, K. Baumgärtner, J. Bustos, A. C. Pöpller, A. H. Clark, M. Nyman, C. Streb, M. Anjass, *Angew. Chem.* **2022**, *134*, e2021145

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Research keywords: Water splitting, Hydrogen evolving reaction, Diplatinum complex, TADF

TADF and Photocatalytic Properties of Diplatinum Complex Bridged by *N*-2-Pyridylimidoyl-2-pyridylamidinate

Continuous efforts have been made to develop efficient and stable molecular catalysts for hydrogen evolution reaction (HER) since the end of 1980s. In this context, we have reported for the first time that various kinds of mono- and dinuclear polypyridyl platinum(II) complexes can serve as molecular catalysts for HER in the well-known photosystem made up of EDTA, [Ru(bpy)₃]²⁺, and methylviologen.^[1] Moreover, we have also reported for the first time that [Pt(tpy)Cl]⁺ can act as a photo-hydrogen-evolving molecular device (PHEMD) only in the presence of EDTA.^[2] However, it still remains a challenge to substantially improve the long-term stability and the visible light responsibility of Pt(II)-based PHEMDs. In this study, we have synthesized a novel diplatinum(II) complex, **Pt₂(bpia)** (inset of Figure 1) by using *N*-2-Pyridylimidoyl-2-pyridylamidinate (**bpia**).^[3]

Pt₂(bpia) displays two strong absorptions centered at 314, 378 nm and a weak broad absorption up to ca. 650 nm in an aqueous solution containing of 10 vol% of *N*-methyl-2-pyrrolidone (NMP). The characteristic broad absorption over 450 nm is assignable to the spin-forbidden S-T transitions which are partially allowed due to the relatively strong spin-orbit interaction between two platinum centers, which indicates that the light absorption property of **Pt₂(bpia)** at the visible domain is significantly better than those of the previously reported Pt(II)-based PHEMDs. Besides, **Pt₂(bpia)** exhibits relatively strong luminescence at 642 nm with a substantially longer average lifetime of 105 ns even in H₂O at room temperature. Interestingly, luminescence maxima gradually shift from 646 to 631 nm with decreasing the luminescence intensity by rising the temperature from 0 to 60 °C, which suggests that **Pt₂(bpia)** shows thermally activated delayed fluorescence. **Pt₂(bpia)** shows photocatalytic HER only in the presence of EDTA over 100 h (TON is 93, Figure 1), whereas all the previously reported Pt(II)-based PHEMDs lose their activities within several hours (max TON is 35). Moreover, **Pt₂(bpia)** is found to be the first example of Pt(II)-based PHEMDs promoting photocatalytic HER even under the visible light irradiation over 500 nm.

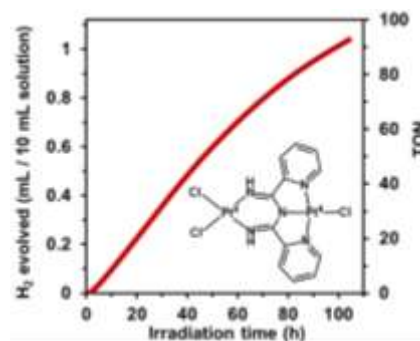



Figure 1. H₂ production from an aqueous acetate buffer solution (0.1 M, pH = 5.0) containing 10 vol% NMP, 30 mM EDTA, 0.1 M NaCl and 0.05 mM **Pt₂(bpia)** under the light irradiation (400 < λ < 800 nm).

[1] K. Sakai and H. Ozawa, *Coord. Chem. Rev.*, **2007**, 251, 2753-2766

[2] R. Okazaki, and K. Sakai, *Dalton Trans.*, **2009**, 6127-6133.

[3] J. Brusso, et al., *Cryst. Growth. Des.*, **2017**, 17, 6572-6578.

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Research keywords: Polyoxometalates, Oxidation catalysis, Aluminum cluster


Title of your talk

Application of Fully Inorganic Porous Ionic Crystals in Oxidation Catalysis

Polyoxometalates (POMs) are anionic oxide clusters widely applied in catalytic materials.^[1] In our laboratory, we have synthesized porous ionic crystals (PICs) solely comprising inorganic units by integrating POM with a cationic inorganic cluster cation, specifically the Keggin-type Al_{13} -oxo cluster ($[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) and reported their catalytic functions.^[2] However, the application of fully inorganic PICs in catalytic reactions has been limited to acid-catalyzed reactions such as pinacol rearrangement and acetalization.^[3] Therefore, this study aims to apply fully inorganic PICs in oxidation catalysis. To impart oxidation catalytic functions to the fully inorganic PICs, we focused on an Anderson-type POM, $[\text{AlMo}_6(\text{OH})_6\text{O}_{18}]^{3-}$ (AlMo_6), known for its redox activity. We synthesized $[\delta\text{-Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}] [\text{AlMo}_6(\text{OH})_6\text{O}_{18}]_2(\text{OH})$ ($\delta\text{-Al}_{13}\text{-AlMo}_6$) by reacting the anionic AlMo_6 with $[\delta\text{-Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ cations in aqueous solution at room temperature. Single-crystal X-ray structural analysis revealed that $\delta\text{-Al}_{13}\text{-AlMo}_6$ forms a one-dimensional nanochannel approximately $8 \times 4 \text{ \AA}$, with $\delta\text{-Al}_{13}$ and AlMo_6 layers stacked along the b-axis. PXRD and IR analysis suggested that $\delta\text{-Al}_{13}\text{-AlMo}_6$ can be synthesized as a bulk powder. Using $\delta\text{-Al}_{13}\text{-AlMo}_6$ as a solid catalyst, we conducted the oxidation of 2-chloroethyl ethyl sulfide (CEES) in EtOH solvent under H_2O_2 , showing a high conversion rate of CEES (>99%, reaction time: 25 min) even at room temperature. Similarly, the oxidation of methionine under H_2O_2 in aqueous solution also resulted in a high conversion rate of methionine (>99%, reaction time: 15 min) at room temperature. The reaction mechanism based on the results of control experiments using other catalysts and spectroscopic measurements will be discussed.

Reference.

- [1] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science*. **2003**, 300, 964–966.
- [2] W. Zhou, N. Ogiwara, Z. Weng, N. Tamai, C. Zhao, L. Yan, S. Uchida, *Chem. Commun.* **2021**, 57, 8893–8896.
- [3] N. Ogiwara, S. Uchida, *Chem Catal.* **2023**, 3, 100607.

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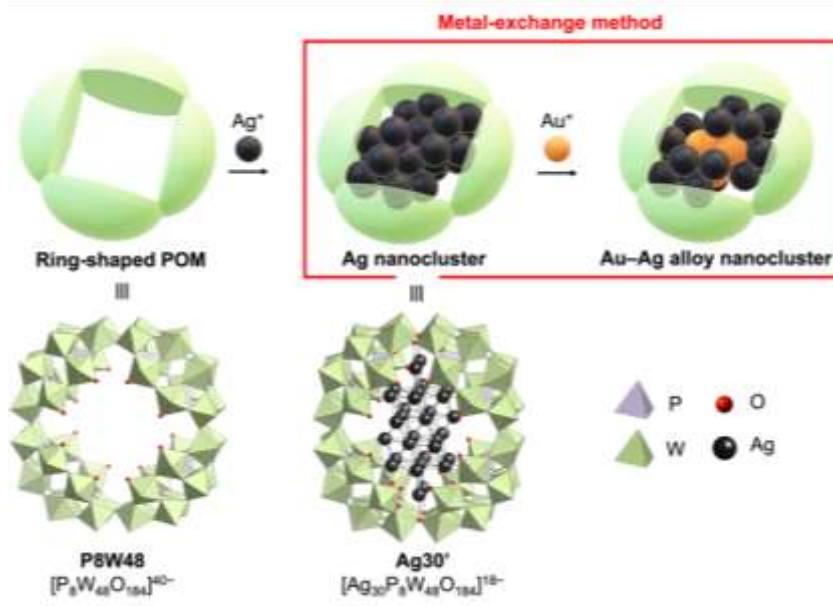
Research keywords: lacunary polyoxometalate, noble metal nanocluster


Synthesis of Au–Ag Alloy Nanoclusters Using Ring-Shaped Polyoxometalates

Alloying plays an important role in a development of metal nanocluster chemistry because alloy nanoclusters show diverse structures, electronic states, and physicochemical properties. Recently we developed the synthetic method of silver nanoclusters using polyoxometalates (POMs) as templating ligands that possess unique synergetic and/or cooperative physicochemical properties. Above all, surface-exposed $\{Ag_{30}\}$ nanoclusters (**Ag30'**) encapsulated within a ring-shaped POM $TBA_{12}H_{28}[P_8W_{48}O_{184}]^{40-}$ (TBA = tetra-*n*-butylammonium; **P8W48**) exhibited high catalytic activity owing to their exposed Ag surface easily accessed by the substrate^[1]. However, the synthetic method was hardly applicable to alloy nanoclusters and the successful synthesis of the metal nanocluster using POMs as ligands was limited to Ag nanocluster. Herein, we successfully synthesized gold-silver alloy nanocluster stabilized by **P8W48**. The reaction of **Ag30'** and Au(I) complex lead to the formation of Au-Ag alloy nanocluster via metal exchange method. Based on X-ray crystallographic and elemental analyses, it was revealed that Au-Ag nanocluster had Au-core Ag-shell structure. X-ray absorption fine structure study was also conducted to investigate the structure and electronic state. Ag K-edge *R*-space extended X-ray absorption fine structure (EXAFS), Au L₂-edge EXAFS, and curve-fitting analysis of Au-Ag alloy nanocluster clearly showed the incorporation of Au atoms into Au-Ag alloy structures.

References.

- [1] K. Yonesato, D. Yanai, S. Yamazoe, D. Yokogawa, T. Kikuchi, K. Yamaguchi, K. Suzuki, *Nat. Chem.* **2023**, *15*, 940–944.



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Research keywords: Qubit; Dawson-type tungstate; $S=1/2$ copper(II)

Spin-lattice relaxations of a $S=1/2$ copper(II)-substituted Dawson-type phosphotungstate

Mononuclear $S=1/2$ complexes have recently attracted attention as a potential quantum bit (qubit) for quantum computation [1]. Since the lifetime of superposition (coherence) of the spin state is governed by spin-lattice relaxation time, compounds showing long longitudinal relaxation are valuable. Dawson-type POMs have a large molecular skeleton, which is expected to reduce magnetic dipole interaction and promote magnetic relaxation time. In this presentation, we report magnetic relaxation phenomena of a $S=1/2$ copper(II)-substituted Dawson-type phosphotungstate $\text{K}_8[\text{P}_2\text{W}_{17}\text{O}_{61}\text{Cu}(\text{H}_2\text{O})] \cdot 15\text{H}_2\text{O}$ [2].

The electron spin resonance (ESR) spectrum of magnetically diluted sample $\text{K}_8[\text{P}_2\text{W}_{17}\text{O}_{61}\text{Cu}_{0.05}\text{Zn}_{0.95}(\text{H}_2\text{O})] \cdot 15\text{H}_2\text{O}$ showed four fine splitting and one large peak due to the interaction between nuclear spin $I=3/2$ ($^{63,65}\text{Cu}$) and electronic spin $S=1/2$ [3].

The AC susceptibility measurements of 5% magnetically diluted powder of **dil.1** showed slow magnetic relaxation in an applied static magnetic field H_{dc} (Figure 1). The longest relaxation time was 91 ms (1.8 K and $H_{\text{dc}}=5000$ Oe). The relaxation time for the copper(II)-substituted 5% magnetically diluted sample of Keggin-type silicotungstate at the same condition became shorter (64 ms at 1.8 K and $H_{\text{dc}}=5000$ Oe). We conclude that the large Dawson-type skeleton effectively reduces intermolecular interaction and affords longer longitudinal relaxation time.

A part of this work was conducted at the Institute for Molecular Science. We also acknowledge the JSPS Core-to-Core program (International Network in Polyoxometalate Science for Advanced Functional Energy Materials).

References

- [1] R. Sessoli *et al.*, *J. Am. Chem. Soc.*, **2016**, *138*, 11234.
- [2] R. G. Finke *et al.*, *J. Am. Chem. Soc.*, **1991**, *113*, 7209.
- [3] A. M. V. Cavaleiro *et al.*, *Polyhedron*, **1999**, *18*, 1163.

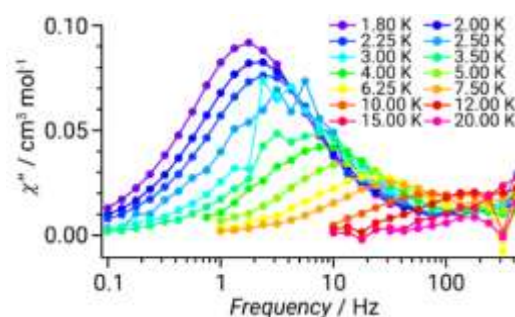



Figure 1 The out-of-phase signal of **dil.1** measured in $H_{\text{dc}}=5000$ Oe

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Research keywords: CO₂ reduction, copper(I) photosensitizer, ionic interaction, photocatalysis in aqueous media

Controlling the Photofunctionality of a Copper(I) Photosensitizer for Photocatalytic CO₂ Reduction in Aqueous Media

To suppress global warming and undesirable climate changes, photocatalytic CO₂ reduction into useful chemical fuels has attracted considerable attention in recent years. With this aim, our group previously reported highly efficient and selective photocatalytic CO₂-to-CO conversion using a water-soluble copper(I) photosensitizer (**CuPS³⁻**) and a cobalt porphyrin catalyst (**CoTMPyP**) in fully aqueous media (**Figure AB**).^[1-2] In this study, ion-pair formation of a trianionic copper(I) photosensitizer, **CuPS³⁻** with alkylammonium cation, hexamethonium (**HM²⁺**), is found to effectively lead to the increase in luminescence lifetime and quantum yield due to the suppression of non-radiative decay induced by water solvates ($\tau_{ave} = 0.89 \rightarrow 15 \mu\text{s}$, $\Phi_{em} = 0.013 \rightarrow 0.11$).^[3] Interestingly, the ion-pair formation results in the substantial enhancement in the electron transfer efficiency and photocatalytic CO₂-to-CO conversion (**Figure C**).

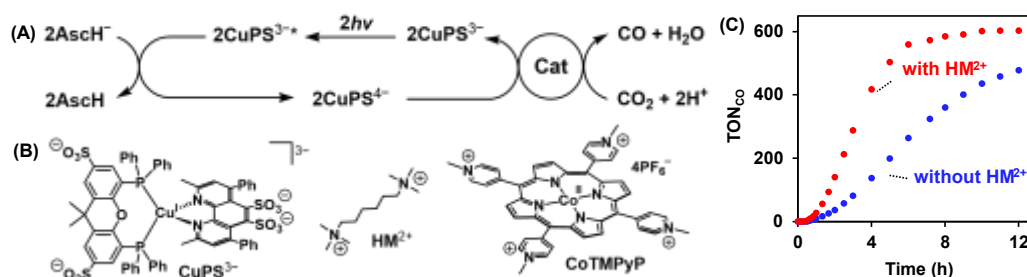



Figure (A) Photocatalytic CO₂ reduction driven by **CuPS³⁻**. (B) The structure of **CuPS³⁻**, **HM²⁺** and **CoTMPyP**. (C) Photocatalytic activities for CO formation in the presence (red) or absence (blue) of **HMCl₂** (50 mM). Photolysis was carried out in CO₂-saturated NaHCO₃ solution (0.1 M, pH = 6.7) solution (5 mL) containing **CoTMPyP** (5 μM), **CuPS³⁻** (0.5 mM) and AscHNa (5 mM) at 25 °C under Xe lamp irradiation ($\lambda > 400 \text{ nm}$, 300 mW cm⁻²).

References

- [1] X. Zhang, M. Cibian, A. Call, K. Yamauchi, K. Sakai, *ACS Catal.*, **2019**, *9*, 11263-11273.
- [2] X. Zhang, K. Yamauchi, K. Sakai, *ACS Catal.*, **2021**, *11*, 10436-10449.
- [3] F. Sueyoshi, X. Zhang, K. Yamauchi, K. Sakai, *Angew. Chem. Int. Ed.*, **2023**, *62*, e202217807.

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Research keywords: Photocatalytic water oxidation, cobalt polyoxometalate, Carbon nitride

Highly Efficient Photocatalytic Water Oxidation by Carbon Nitride Modified with an Anderson Type Cobalt Polymolybdate Catalyst

Recently, studies on solar energy conversion by using semiconductor photocatalysts have attracted considerable attention. Among numerous n-type semiconductors, graphitic carbon nitride (g-C₃N₄ [1], Figure 1) has been extensively studied as a promising semiconductor for artificial photosynthesis because the conduction band edge is relatively more negative than metal oxides (TiO₂, WO₃, etc). However, the photocatalytic water oxidation by g-C₃N₄ modified with a molecular water oxidation catalyst (WOC) is very limited due to the insufficient driving force (ca. 600 meV) for the water oxidation driven by molecular WOCs [2].

In this study, Anderson type monocobalt polymolybdate (**CoPOM**³⁻ [3], Figure 1) and cobalt tetraphenylporphyrine (**CoTPP** [4]) were utilized as a molecular WOC for g-C₃N₄ photocatalyst. At first, a water insoluble **CoPOM**³⁻ ((THA)₃**CoPOM**, THA⁺ = tetraheptylammonium) and **CoTPP** were physisorbed over the g-C₃N₄ by impregnation method. Electrochemical measurements of FTO electrodes modified with g-C₃N₄/(THA)₃**CoPOM** or g-C₃N₄/**CoTPP** revealed the onset overpotentials for water oxidation to be 490 and 590 mV. These results proved the photocatalytic water oxidation by g-C₃N₄/(THA)₃**CoPOM** or g-C₃N₄/**CoTPP** is thermodynamically favorable. The photocatalytic performances of g-C₃N₄/(THA)₃**CoPOM** and g-C₃N₄/**CoTPP** for water oxidation were evaluated in the presence of Ag⁺ as a sacrificial electron acceptor at pH 8.7. Interestingly, g-C₃N₄/(THA)₃**CoPOM** shows better photocatalytic activity than g-C₃N₄/**CoTPP** even though the loading amount of WOCs were adjusted to be the same (25 μmol/g). The obtained TON_{7h} (57.8) and TOF (15.8 h⁻¹) based on the loading amount of (THA)₃**CoPOM** were found to be the highest among the previous reports.

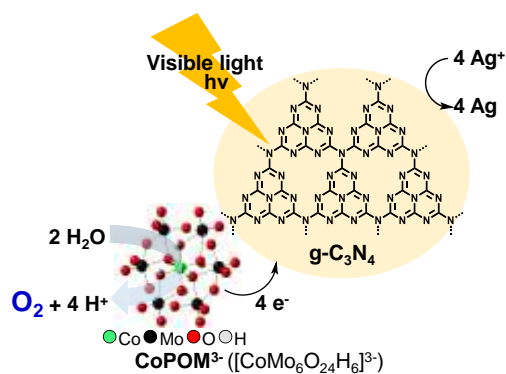



Figure 1. schematic representation of the photocatalytic water oxidation by g-C₃N₄/(THA)₃**CoPOM**

References

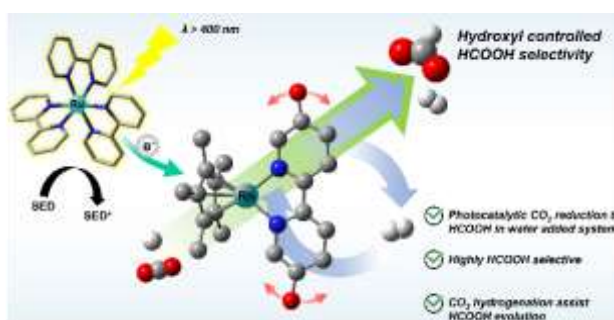
- [1] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76-80.
- [2] Z. Luo, M. Zhou, X. Wang, *Appl. Catal. B*, **2018**, 238, 664-671.
- [3] S. Tanaka, M. Annaka, K. Sakai, *Chem. Commun.*, **2012**, 48, 1653-1655.
- [4] T. Nakazono, A. R. Parent, K. Sakai, *Chem. Commun.*, **2013**, 49, 6325-6327.

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Research keywords: Photocatalysis, CO₂ reduction, Rhodium complex, visible light, formic acid, DFT studies

Controlling Formate Selectivity in Photocatalytic CO₂ Reduction: The Role of Hydroxyl Positioning in RhCp*(dihydroxy-bpy) complexes


Towards the establishment of a carbon-neutral society, artificial photosynthesis, replacing fossil fuels with renewable energies (H₂, HCOOH, CH₃OH, etc.), has attracted great attention in recent years¹. One of the most important issues in this area has been to advance our knowledge and technical skills in controlling selectivity of CO₂



reduction to formic acid (HCOOH). However, the complexity of the mechanism of the products in the photocatalytic CO₂ reduction to HCOO⁻ system makes it difficult to control selectivity². Here, we focus on the effects on selectivity and activity of HCOO⁻ evolution by tuning position of hydroxyl in RhCp*(hydroxy-bpy), where HCOO⁻ evolution in high pressure and temperature condition of aqueous solution has been reported³. When 17% H₂O is added to the solvent, compared to performance in organic solvent, the H₂ evolution activity is reduced and the HCOO⁻ evolution activity significantly increased, Sel_{HCOOH}=14% to Sel_{HCOOH}=83%. This is a result of the change in complex structure stability due to the position of hydroxyl in the ligand and the effect of CO₂ hydrogenation using H₂ generated by photocatalytic reaction. Also, we propose specific insights into the mechanism of HCOO⁻ evolution from free energy change diagram of RhCp*(DHBP) calculated by DFT. Meta-stable state free HCOO⁻ evolution process via hydride jump, rather than traditional mechanism via simultaneous interaction with metal and proton of CO₂, is confirmed by IRC calculations and suggests a new possibility for HCOO⁻ evolution mechanism where both Cp* and rhodium are protonated by proton transfer. Moreover, significant increase in activity and selectivity of HCOO⁻ through H₂O addition is rare case and suggests a strategy of developing an effective photocatalytic CO₂ reduction to HCOO⁻ system in fully aqueous media.

Reference.

- [1] Rogelj, J.; Eelzen, M. D.; Höhne, N.; Fransen, T.; Fekete, H.; Winkler, H.; Schaeffer, R.; Sha, F.; Riahi, K.; Meinshausen, M. Paris Agreement Climate Proposals Need a Boost to Keep Warming Well Below 2 °C. *Nature* **2016**, 534, 631–639.
- [2] Elgrishi, N.; Chambers, M. B.; Wang, X.; Fontecave, M. Molecular Polypyridine-Based Metal Complexes as Catalysts for the Reduction of CO₂. *Chem. Soc. Rev.* **2017**, 46 (3), 761–796.
- [3] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara and K. Kasuga, Simultaneous Tuning of Activity and Water Solubility of Complex Catalysts by Acid-Base Equilibrium of Ligands for Conversion of Carbon Dioxide. *Organometallics*, **2007**, 26, 702–712.

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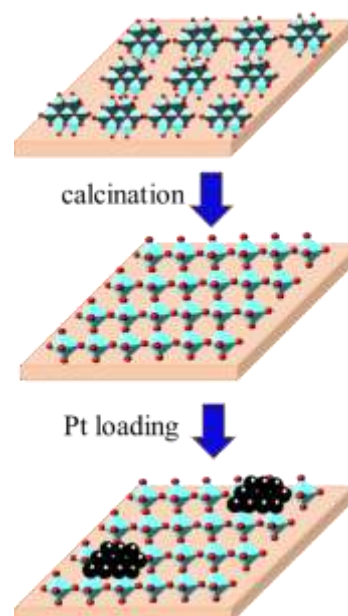
Research keywords: CO₂ hydrogenation, Low-temperature catalytic reaction system, Electric field

Polyoxometalate-derived MoO_x-based catalyst for CO₂ hydrogenation

A reverse water gas shift (RWGS) reaction of CO₂ to chemically useful CO is a promising process for CO₂ valorization. However, the RWGS required high reaction temperature above 600 K to obtain the high CO₂ conversion because of thermodynamic limitation. We applied an unconventional reaction system which catalytic reactions occur even at low temperature under an electric field. This reaction system achieved the RWGS reaction even below 500 K [1]. In addition, MoO_x species with Pt were active for CO₂ hydrogenation [2,3] and metal oxide prepared from polyoxometalate catalyzed several redox reactions under the electric field at low temperatures [4]. Therefore, we focused on development of the new polyoxometalate-derived MoO_x-based catalysts which exhibit high catalytic performance for the low temperature RWGS reaction under the electric field.

MoO_x-based catalysts were prepared by a successive impregnation method [3]: MoO_x/MO were obtained from a calcination of Anderson-type heptamolybdate supported various metal oxide supports (MO: MgO, Al₂O₃, TiO₂, Nb₂O₅, ZrO₂, CeO₂) at 773 K, and then, Pt was loaded on the MoO_x/MO and reduced at 573 K. The prepared catalysts were characterized by XRD, SEM-EDX, TG-DTA. The activity tests of them were carried out for RWGS reaction.

The Pt/MoO_x/ZrO₂ showed the highest activity for RWGS reaction, with CO₂ conversion rate of 34.9% and CO selectivity of 99.2%, under the electric field below 500 K.



Reference.

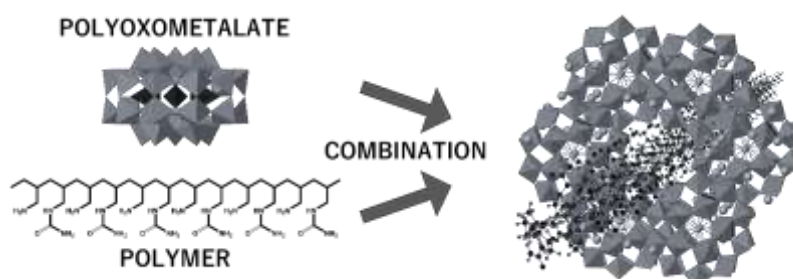
- [1] K. Oshima *et al.*, *Catal. Today*, 232, 27-32 (2014).
- [2] H. Ge *et al.*, *J. Mater. Chem. A*, 9, 13898-13907 (2021).
- [3] T. Toyao *et al.*, *ACS Catal.*, 9, 8187-8196 (2019).
- [4] K. Sugiura *et al.*, *Sci. Rep.*, 6, 25154 (2016).

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Research keywords: polyoxometalate, polymer, proton conductivity, urea, ammonium

Solid Proton Conductors with High Performance Based on Composites of Sodium-centered Phosphotungstate and Urea-modified Polyallylamine

Regarding that rational functionality for electrolytes demands both designability and structural stability, this work focuses on hybrid materials merging inorganic and organic components. The inorganic component, polyoxometalate (POM), is chosen due to its negatively charged molecular surface which facilitates the mobility of counter cations (H^+ ions, etc.).^[1] Also, hybrid materials are anticipated to gain a robust structure from the crystalline form. Meanwhile, on a molecular level, organic polymers, modifiable with various functional groups, enable control over carrier density which in turn affects proton mobility. Besides, concomitant hydrogen-bonding networks contribute to structural stability.^[2]




Here, three POM-polymer composites (NaPU25, NaPU50 and NaPU75) are successfully synthesized by combining sodium-centered Preyssler-type POM ($K_{14}[Na(H_2O)P_5W_{30}O_{110}]$) and urea-modified polyallylamine (UPAA) at modification ratio of 0.25, 0.50 and 0.75, respectively. Furthermore, proton conductivity performance is evaluated by electrical impedance methods. In particular, NaPU50 exhibits high proton conductivity of $1.85 \times 10^{-2} \text{ S cm}^{-1}$ at 75 °C and 75% relative humidity (RH). Additionally, multiple spectroscopic studies are conducted to characterize the composites and establish the correlation between proton conductivity and urea modification ratio. The conclusion is drawn that ammonium ions produced during the combination process serve as crucial proton carriers.

Reference.

[1] M. R. Horn *et al.*, *Energy Environ. Sci.*, 2021,14, 1652-1700

[2] S. J. D. Lugger *et al.*, *Chem. Rev.* 2022, 122, 5, 4946–4975

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Research keywords: organic–polyoxometalate hybrids, porphyrin, photocatalyst

Porphyrin–Polyoxotungstate Molecular Hybrids with Highly Active and Durable Photocatalysis

The development of organic–polyoxometalate (POM) hybrids has recently received considerable interest because of their unique properties derived from the synergy effects of each component. Porphyrins are promising building units for these hybrids because of their strong visible light absorption and the ability to generate reactive singlet oxygen ($^1\text{O}_2$). However, porphyrins are

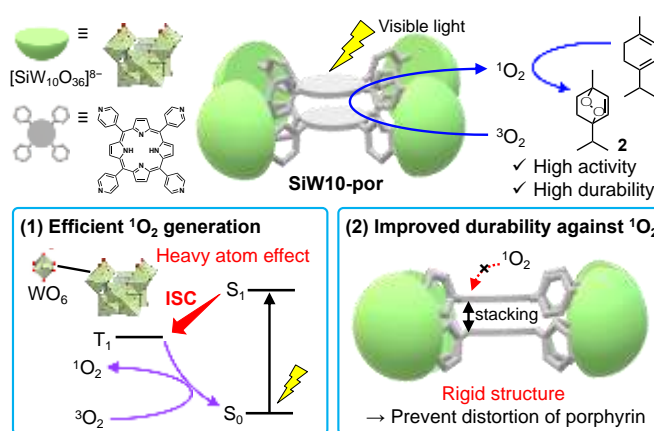



Figure 1. Outline of this study.

degraded by $^1\text{O}_2$ attacking to the meso-position.^[1] To address this challenge, this study focuses on porphyrin–POM hybrids featuring a stacking porphyrin dimer (Figure 1). The presence of multiple heavy atoms in POM frameworks is expected to facilitate intersystem crossing (ISC) from the photoexcited singlet state to the triplet state for promoting efficient formation of $^1\text{O}_2$. In addition, the rigid hybrid structures, resulting from the coordination of POMs and porphyrin π - π stacking, can prevent the distortion of porphyrin rings by addition of $^1\text{O}_2$ and are expected to exhibit high durability against $^1\text{O}_2$. In this study, we developed a porphyrin–polyoxotungstate molecular hybrid (**SiW10-por**) that exhibited remarkable efficiency and durability for visible-light-responsive aerobic oxidation.^[3]

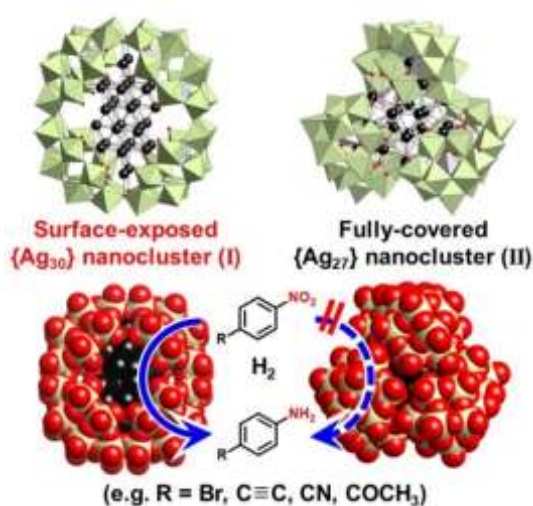
In the presence of a catalytic amount of **SiW10-por** (0.003 mol%), α -terpinene (**1**) was selectively converted to ascaridole (**2**) by irradiation with visible light using $^3\text{O}_2$ as the oxidant. The reaction hardly proceeded when using **PMo10-por**^[2] that composed of polyoxomolybdates instead of polyoxotungstates. Notably, the photocatalytic activity of **SiW10-por** and the quantum yield of $^1\text{O}_2$ formation by **SiW10-por** were higher than that of free porphyrin likely because of the heavy atom effect of POMs. Furthermore, **SiW10-por** exhibited remarkable durability against the generated $^1\text{O}_2$ in comparison to free porphyrin under photo-irradiation despite its high efficiency of $^1\text{O}_2$ generation. References. [1] R. Bonnett, G. Martinez, *Tetrahedron* **2001**, *57*, 9513. [2] C. Li, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2021**, *60*, 6960. [3] M. Yamaguchi, *et al.* manuscript in revision.

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Research keywords: silver nanocluster, ring-shaped polyoxometalate, catalytic hydrogenation

Synthesis and Properties of Surface-Exposed Ag Nanoclusters within Ring-Shaped Polyoxometalates


Silver (Ag) nanomaterials that possess interfaces with metal oxides are attractive catalyst materials because of the unique reactivity on their surfaces. We have developed structurally well-defined hybrid molecules of polyoxometalates (POM) and Ag nanoclusters that exhibit cooperative properties such as hydrogen dissociation and photocatalysis.^[1] However, the surfaces of these Ag nanoclusters were completely covered by POMs, limiting their applications as catalysts. In this study, we synthesized structurally well-defined {Ag₃₀}



nanoclusters with exposed Ag surface (**I**) within a ring-shaped POM (**P8W48**) via sequential reaction of **P8W48** with Ag⁺ ions and a reducing agent.^[2] Compound **I** showed high stability despite its exposed Ag surface both in solution and in solid state. **I** exhibited high catalytic activity for the selective reduction of nitroarenes to the corresponding anilines under mild reaction conditions. Furthermore, the structure of **I** was remained even after the catalytic reduction of nitrobenzene. On the other hand, the reaction hardly proceeded with Ag nanocluster covered by POM (**II**). In addition, we revealed that **I** dissociated 3 molecular hydrogens into 6 protons and 6 electrons. These results suggest that the high catalytic performance and specific selectivity was achieved owing to unique H₂ dissociation and the exposed surface of Ag nanocluster.

Reference.

[1] (a) K. Yonesato, H. Ito, H. Itakura, D. Yokogawa, T. Kikuchi, N. Mizuno, K. Yamaguchi, K. Suzuki, *J. Am. Chem. Soc.* **2019**, *141*, 19550; (b) K. Yonesato, S. Yamazoe, D. Yokogawa, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2021**, *60*, 16994; [2] K. Yonesato, D. Yanai, S. Yamazoe, D. Yokogawa, T. Kikuchi, K. Yamaguchi, K. Suzuki, *Nat. Chem.* **2023**, *15*, 940.

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Research keywords: framework, latent heat, amorphization, PCMs

Structural transformation with large latent heat in {V₁₈}-type polyoxometalates framework

Efficient thermal managements are one of the challenges for today's technology, but thermal and energy materials are still in the developing stages. Substance that absorbs (releases) a large amount of heat during a phase change is known as a phase change material (PCM). Among them, there are two major types of PCMs that use latent heat: one is a solid-to-liquid change (SLPCMs), and the other is a solid-to-solid change (SSPCMs). SLPCMs has a larger heat density than SSPCMs, however liquid-based systems are not friendly for electronic devices. A new system with the both advantages of SLPCMs and SSPCMs is required for next generation electronics with excessive waste heat.

Herein, we were interested in a water cluster containing polyoxometalate-based $A_x[\{M(OH_2)_4\}_3V_{18}O_{42}(SO_4)] \cdot n(H_2O)_6$ (**1-M**: M = Mn, Fe, Co, Ni, Cu, Zn, Cd). This compounds, for example **1-Ni**, compound of {V₁₈} cluster linked with $[Ni(OH_2)_4]^{2+}$ at the both axial coordination sites, forming -POM-Ni(OH₂)₄-POM- cubic framework with four water hexamers ($n \sim 4$). We investigated temperature developments and thermal properties of the **1-M** by temperature variable powder XRD (TV-PXRD), TG-DTA and complex permittivity.

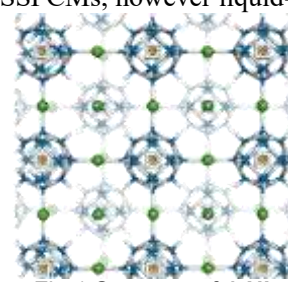



Fig.1 Structure of **1-Ni**

TG-DTA and TV-PXRD results show desorption of water hexamers around room temperature at which **1-M** transformed to amorphous. It is considered from the framework structure is collapsed by water molecules desorbed. However, water moisture treatment backed amorphous to crystalline phase whose XRD patterns corresponds to that of original crystal, showing crystal-to-amorphous-to-crystal (CAC) process. The enthalpy change determined by DTA was 37 kJ per water molecule for **1-Ni**, which is comparable to evaporation heat of water ~ 45 kJ/mol. All of other **1-M** are isostructural to **1-Ni** with subtle differences in lattice length due to those of ionic radius of M. Similar CAC process and ΔH were observed for a set of **1-M**, indicating that net enthalpy change upon CA transformation was governed by hydrogen bond of the water hexamer.

In conclusion CAC transformation of the **1-M** was investigated and we revealed a large enthalpy change comparable to that of evaporation heat of water without liquid phase.

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Research keywords: Metal Free Perovskite, Solid Solution, Mechanochemical Synthesis

Mechanochemical Synthesis of Perovskite-type Molecular Solid Solution (H₂dabco,H₂hmta)(NH₄)(BF₄)₃; Composition Dependence of Structure

ABX₃ perovskite structure is widely utilized for platform of functional materials such as ferroelectrics, solar-cell and battery materials and their structure, since closed packing structure of the ternary system, is understood by ionic radius of A, B and X. Solid solution of different ions but with comparable radii have been developed for fine tuning of physical and chemical properties, and also for discovery of a new phase.

In this manuscript, we report solid-solutions of molecular perovskite (AA')NH₄X₃ by mixing organic cation with comparable size but different molecular symmetry prepared by mechanochemical process. This is perovskite structure, but metal-free ANH₄X₃ with organic cation A and ammonium and monovalent anion such as halide. [1] They are spot-lighted due to an expectation as environmental and human-friendly functional materials for global sustainable development, however solid solution is less developed due to different type of organic molecule in the lattice.

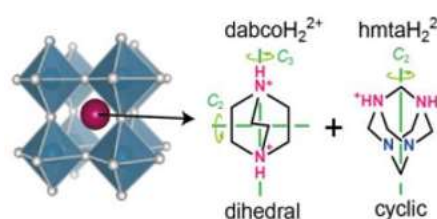



Fig. 1. Schematic picture of AA'(NH₄)X₃ perovskite

Herein, we applied mechanochemical method to prepare solid solution of the molecular perovskite (AA')NH₄X₃. By grinding dabco, hmta (figure 1) under the addition of HBF₄ and ammonium, solid solutions (H₂dabco_{1-x},H₂hmta_x)(NH₄)(BF₄)₃ were obtained. By temperature variable powder-XRD, DSC and solid-state NMR measurements, we revealed solution ratio *x* dependence on phase transition temperature and also morphotropic phase boundary around *x* ~0.5 at which space group and molecular dynamics of the A site organic cation differs from both *x* = 0 and 1. It was revealed that mechanical method is one of the possible candidates for the prepare solid solution of metal free molecular perovskites.

Reference.

[1] R. Tsunashima et al., *Angew. Chem. Int. Ed.*, **58**, 9184-9187 (2019).

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Research keywords: molecular aluminum oxo-hydroxo cluster

Synthesis and catalysis of organic solvent-soluble molecular aluminum oxo-hydroxo clusters

Aluminum oxide (alumina) is widely used as a Lewis acid catalyst because of its heat resistance, high specific surface area, Lewis acidity. In addition, alumina is low cost due to the abundance of aluminum minerals in the earth's crust.^[1] Recently, it has been discovered that 5-

coordinated Al sites of bulk alumina play an important role to achieve highly active Lewis acid catalysts and/or supports.^[2] However, surface structure of bulk alumina is unclear, thus making it difficult to control the surface structure at an atomic level and to construct highly catalytically active 5-coordinated Al sites. Therefore, it is desirable to develop that development of new catalysts with high ratio of 5-coordinated Al sites and to control the active sites. Molecular alumina clusters are cationic oxo-hydroxo clusters formed by the condensation of aluminum hydroxide and possess the similar surface structures to those of alumina. Most of studies on molecular alumina clusters ranges synthesis and characterization of new clusters. Since the molecular structures of these clusters can be finely tailored at an atomic level, it is expected to exhibit excellent catalytic activity. However, unlike bulk alumina and aluminum hydroxide, molecular aluminum clusters have not been studied as catalysts presumably because they are gelatinized or isomerized in water. Therefore, we focused on stable $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (**Al₁₃**) and envisaged that development of an organic solvent-soluble **Al₁₃** could achieve unique homogeneous catalyst in organic media by mimicking the surface structure of bulk alumina. In this study, we synthesized and characterized new arylborate salts of **Al₁₃** which was synthesized by the Grignard reaction, by a metathesis reaction of the **Al₁₃** clusters with the arylborate salts (Figure 1). The organic solvent-soluble **Al₁₃** was successfully synthesized for the first time, and could be used as a Lewis acid catalyst in organic media.

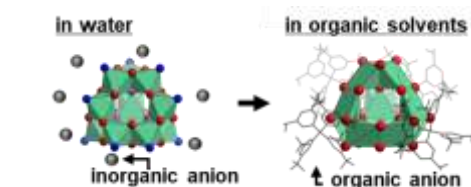



Figure 1. Schematic of the synthesis of organic solvent-soluble **Al₁₃**.

Reference.

[1] I. Bezverkhy P. Afanasiev, C. Geantet, M. Lacroix, *J. Catal.* **2001.** 204, 495–497.

[2] K. Khivantsev, N. R. Jaegers, J. Kwak, J. Szanyi, L. Kovarik, *Angew. Chem. Int. Ed.* **2021.** 60, 17522–17530.

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Research keywords: (single-molecule electret, ferroelectric materials, potassium)

Evaluating dielectric properties of wheel-shape polyoxometalate and inner cations exchange effect

Ferroelectric materials have permanent polarization in their ferroelectric phase. This property is caused by long-range order of dipole-dipole interactions between molecules or atoms, and is therefore considered as a bulk property. However, we reported single-molecule electret (SME) which behaves like a ferroelectric material without intermolecular interactions.^[1] These behaviors were observed in Preyssler-type polyoxometalate (Fig.1). This molecule incorporates a terbium ion (Tb^{3+}) that has two stable sites in a cavity, so molecular polarization occurred according to the position of Tb^{3+} ion. In dielectric measurements, ferroelectric materials show a peak at the phase transition temperature. In addition, they showed a polarization vs. electric field (P-E) hysteresis in the ferroelectric phase *i.e.* below the transition temperature. However, from the temperature dependence of the dielectric properties measurements, phase transition was not observed in SME, up to 400 K. On the other hands, SME showed P-E hysteresis, so this molecule behave like ferroelectric materials without long-range order (Fig.2), near room temperature.

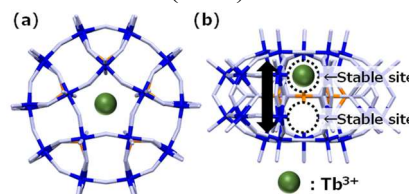


Fig.1. (a)Top and (b)side view of Preyssler-type POM.

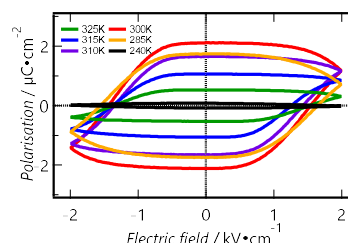


Fig.2. P-E loops of SME.

In my research, I focused on wheel-shape polyoxometalate $K^+ \subset W48$ that incorporates eight potassium ions (purple and pink sphere in Fig.3).^[2] As four of them delocalize between two stable sites in a cavity, this molecule will behave as a new SME. From the temperature dependence of the dielectric constant measurements, ferroelectric phase transition was not observed up to 450 K, like previous SMEs. On the other hands, this molecule showed P-E hysteresis from 300K to 450 K. For these reasons this molecule will behave as a high temperature SME. In addition, the inner cations can be exchanged to NH_4^+ ions, slightly affecting the dielectric properties. In my presentation, I will introduce dielectric properties of $K^+ \subset W48$, ion exchanging process, and the inner ions dependence of the dielectric properties.

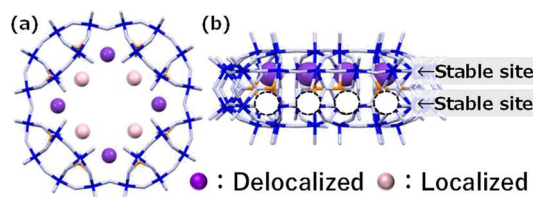
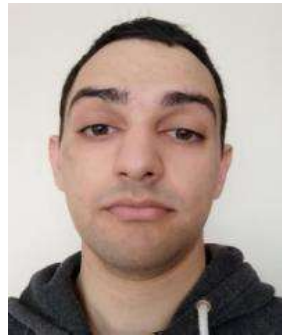


Fig.3. (a)Top and (b)side view of $K^+ \subset W48$.

Reference.

[1] C. Kato, S. Nishihara, *et al.*, *Angew. Chem. Int. Ed.*, **2018**, *57*, 13429-13432.

[2] R. Contant, *et al.*, *Inorg. Chem.*, **1985**, *24*, 4610-4614.

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Research keywords: Polyoxometalates, Lindqvist, Transition-metal.

A versatile approach to reactive $\{MW_5\}$ polyoxometalates

Abstract

Investigations of heterometal-substituted POMs have mainly involved Keggin-type anions, due to their relative ease of handling and synthesis.[1,2] We are interested in the effects of the different coordination parameters imposed on sites within the Lindqvist structure, and our efforts to optimise the non-aqueous synthesis of substituted Lindqvist-type polyoxometalates (POMs) $[MW_5O_{18}]^{n-}$ will be described.

Previous work in our group successfully produced cobalt-substituted Lindqvist POMs $(TBA)_6[(CoW_5O_{18}H)_2]$ and $(TBA)_3[(py)CoW_5O_{18}]$ *via* non-aqueous hydrolysis of $(TBA)_2WO_4$ and $WO(OMe)_4$. [3] A variation on the method involving base degradation of $(TBA)_2[W_6O_{19}]$ has now led to the Mn- and Fe-substituted analogues, as confirmed by X-ray crystallography. Preliminary cyclic voltammetry experiments have been carried out on the $\{MnW_5\}$ system and work is ongoing to explore access to higher oxidation state heterometals *via* reaction with suitable oxidizing agents. Initial results for M = Cr, Mn, Fe and Co will be reported.

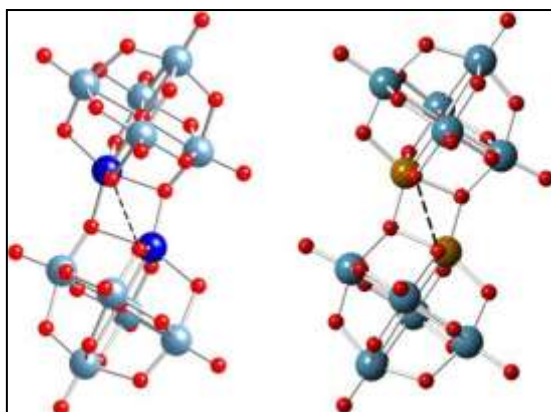


Figure 1 : Structures of $[(MW_5O_{18}H)_2]^{6-}$ for M = Co (left) and Fe (right) showing hydrogen

Reference.

[1] Neumann, R.; Gara, M, *J. Am. Chem. Soc.*, **1995**, *117*, 5066-5074.

[2] Zhang, X. ; Pope, M, *J Mol Catal A Chem*, **1996**, *114*, 201-208

[3] R. J. Errington, G. Harle, W. Clegg, R. W. Harrington, *Eur. J. Inorg. Chem.* **2009**, *34*, 5240 – 5246.

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Research keywords: (supramolecular chemistry, polyoxovanadates, electrochemistry, battery applications)

Novel Polyoxovanadates for Energy Storage & Catalytic Applications

This contribution will present recent progress in polyoxovanadate research for energy conversion and storage applications. We developed a new cation metathesis route to transfer the literature-known {V18} architectures from the aqueous to the organic phase leading to several highly redox-active species.^[1] These systems are currently explored for their application in non-aqueous redox-flow batteries in symmetric configuration following concepts reported by the Matson Group.^[2] Furthermore, recent achievements in heterometallic functionalization of lacunary vanadium oxides^[3,4] will be presented, including a discussion on the role of various reaction parameters on the cluster assembly. An outlook into possible areas of applications will be given.

References:

- [1] A. Müller, R. Sessoli, E. Krickemeyer, H. Bögge, J. Meyer, D. Gatteschi, L. Pardi, J. Westphal, K. Hovemeier, R. Rohlfing, J. Döring, F. Hellweg, C. Beugholt, M. Schmidtman, *Inorg Chem*, **1997**, *36*, 5239–5250.
- [2] L. E. Vangelder, A. M. Kosswattaarachchi, P. L. Forrestel, T. R. Cook, E. M. Matson, *Chem Sci* **2018**, *9*, 1692–1699.
- [3] K. Kastner, J. T. Margraf, T. Clark, C. Streb, *Chemistry – A European Journal* **2014**, *20*, 12269–12273.
- [4] Repp, S., Remmers, M., Rein, A.S.J., Sorsche, D., Carella, L., Rentschler, E., Streb, C., *Nat Commun* **14**, 5563 (2023). <https://doi.org/10.1038/s41467-023-41257-y>

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Research keywords: Gel, Heterogeneous catalyst

Polyethylene Glycol Methyl Ether Methacrylate Hydrogel as Carriers of Silicotungstic Acid for Acid Catalytic Reaction in Water.

1. Introduction

Heteropoly acid (HPA) is strong acids in solution and industrially used as acid catalysts in homogeneous and heterogeneous systems. However, HPA is easily soluble in polar solvents, making it difficult to separate and recover. In this study, we investigated the comprehensive immobilization of silicotungstic acid¹⁾ (STA), onto a triethylene glycol methyl ether methacrylate (TEGMA) gel, a polymer with an ether structure in the side chain²⁾. Because the ether has a high affinity with HPA and is used as an extraction solvent for HPA. STA is immobilized by hydrogen bonding with the ether group of the polymer, and at the same time, aggregation of STA is expected to be suppressed by the polymer network.

2. Experimental methods

STA, TEGMA monomer, and cross-linker Triethylene Glycol Dimethacrylate (TEGDMA) were mixed, and STA/TEGMA composite was synthesized by radical polymerization at 50°C. After synthesis, the composite was washed with distilled water for 24 hours and dried. The crystallinity and dispersibility of STA in the composite, STA content of the composite, and structural stability of the composite were investigated by X-ray analysis (XRD), thermogravimetric analysis (TGA), and Fourier transform infrared spectrometry (FTIR), respectively. The catalytic performance was evaluated by hydrolysis of ethyl acetate in D₂O by proton NMR.

3. Results and discussions

3.1 Evaluation of crystallinity and dispersibility of the composite

No diffraction peaks of STA were observed in any of the composites. It is considered that STA was dispersed and fixed in the gel without crystallization.

3.2 Evaluation of structural stability of the composite

The specific peaks of the STA molecule shown in the figure, 978, 915, 885, and 798 cm⁻¹,³⁾ remain unchanged regardless of the amount of STA loaded. Thus, it is suggested that the structure of STA is not changed during the complex synthesis process. (Fig 1)

3.3 STA loading stability evaluation

STA/TEGMA composites with different initial STA contents were washed with water, and the content was measured by TG. The results showed that up to 40 wt% STA composites maintained the same content after washing, but the content decreased to about 40 wt% for composites with higher initial content.

3.4 Catalytic performance evaluation of the composites

Hydrolysis of ethyl acetate using unfixated STA and the 40 wt% STA composite before and after two washes resulted in more efficient degradation of ethyl acetate absorbed inside the gel, because STA was well dispersed inside the TEGMA gel. (Fig 2) In addition, the reaction stopped when the complex was removed from the ethyl acetate solution during the reaction. Therefore, it is considered that the catalyst was not eluted from the complex during the reaction.

4. Conclusion

Silicotungstic acid (STA) was comprehensively immobilized in a polymer gel with an ether structure in the side chain, and then STA was dispersed and immobilized in the gel without crystallization. Up to 40 wt% of STA was not eluted even after washing, indicating that the catalytic activity was maintained.

References

- 1) R. Himmelmann *et al.*, *Catal. Sci. Technol.* **11**, 3098-3108 (2021)
- 2) J. Zhu *et al.*, *Mater. Adv.* **2**, 3556-3559 (2021)
- 3) K.M. Parida *et al.*, *J. Mol. Catal. A Chem.* **275**, 17, 77-83 (2007)

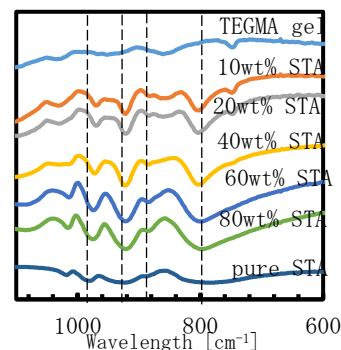


Fig.1 FT-IR patterns of pure STA and STA/TEGMA composites

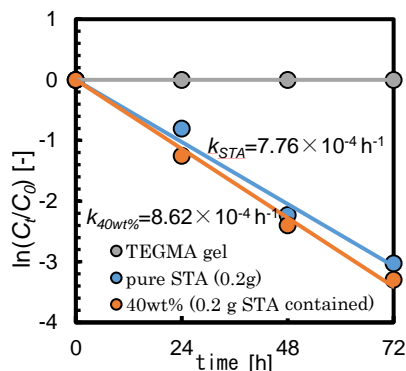


Fig.2 Concentration changes of AcOEt catalyzed by 40wt% STA/TEGMA composites

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Research keywords: (NMR spectroscopy, self-assembly, polyoxovanadates, functionalization)

NMR Spectroscopy as a Powerful Tool for Polyoxovanadate Investigations

NMR spectroscopy is one of the most powerful tools in the field of analytical chemistry which provides one- and two-dimensional spectra to investigate structural features, relaxation times and diffusion coefficients for a variety of different NMR active nuclei. [1] However, there are still many opportunities to increase the use of multicore NMR studies in polyoxometalate chemistry. This is particularly true for the chemistry of functionalized polyoxovanadates where ^{51}V nuclei for V(V) centres can give excellent structural information on timescales comparable to ^1H NMR. In addition, to-date, more complex analyses such as exchange spectroscopy (EXSY), correlation spectroscopy (COSY) and total correlation spectroscopy (TOCSY) are not employed to their optimum. Here, we give an overview of these possibilities using the dodecavanadate $\{\text{V}_{12}\}$ stabilized by “placeholder” cations as example. [2,3]

References:

- [1] Zerbe, O.; Jurt, S. Applied NMR Spectroscopy for Chemists and Life Scientists; WILEY-VCH Verlag GmbH & Co. KGaA, 2014.
- [2] K. Kastner, J. T. Margraf, T. Clark, C. Streb, Chem. Eur. J. 2014, 20, 12269-12273.
- [3] Repp, S., Remmers, M., Rein, A.S.J. *et al.*, Nat Commun. 2023, 14, 5563

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Supramolecular interactions between Polyoxometalates and a Perylene Photosensitizer

Supramolecular organic-inorganic hybrid systems are intriguing materials, due to their great potential as next generation functional materials. Especially in polyoxometalate chemistry the design of new covalent organo-functionalized POMs, enables the application in energy conversion/storage materials. In general, the use of POMs in these areas is mostly based on the electrostatic interaction between a cationic photosensitizer and the polyoxoanion. Here the colloid formation in homogeneous photocatalysis at higher concentrations is a major drawback.^[1] In this study, we explore the assembly of supramolecular aggregates based on the presence of π -stacking interactions.^[2] For this a series of organofunctionalized POMs based on the monolacunary Wells-Dawson polyoxotungstate was synthesized. We deliberately increased the size of the aromatic moieties to study the effects on charge accumulation in presence of a aromatic tetra-substituted Perylenemonoimide dye.

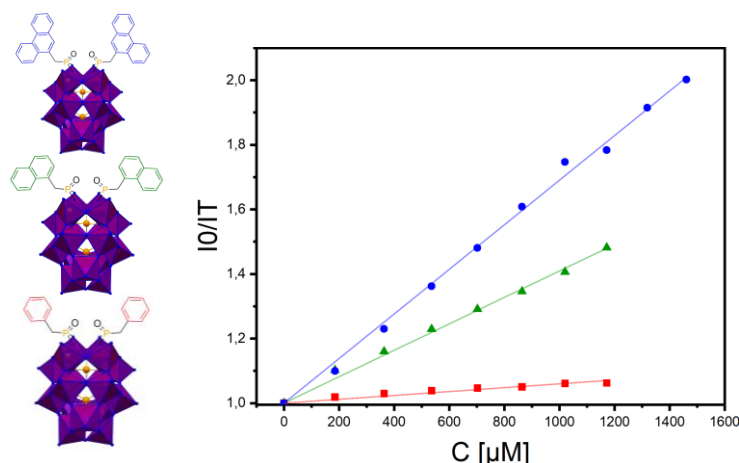


Figure 1: Emission quenching studies of a tetra substituted perylenemonoimide Photosensitizer, with organofunctionalized Wells-Dawson Polyoxotungstates

[1] B. Kirchhoff, S. Rau, C. Streb, *Eur J Inorg Chem* **2016**, 2016, 1425–1429.

[2] S. Knoll, M. Hänle, A. K. Mengele, D. Sorsche, S. Rau, C. Streb, *Chemistry - A European Journal* **2023**, 29,