

## Program

**[17 Dec., 2016]**

**10:00-**            **Opening Remark**            Tatsuo Kimura

### **Invited Lecture I**

10:10-10:35      IL-1: Watcharop Chaikittisilp

10:35-11:00      IL-2: Sunao Kamimura

11:00-11:25      IL-3: Chia-Her Lin

11:25-11:50      IL-4: Kazuhiro Shikinaka

**Lunch: 11:50-13:35**

### **Invited Lecture II**

13:35-14:00      IL-5: Kohji Ohno

14:00-14:25      IL-6: Shiao-Wei Kuo

14:25-14:50      IL-7: Tomohiko Okada

14:50-15:15      IL-8: Tatsuya Nishimura

### **Break**

15:25-15:50      IL-9: Yu-Te Liao

15:50-16:15      IL-10: Dai Mochizuki

16:15-16:40      IL-11: Youn Soo Kim

16:40-17:05      IL-12: Minoru Sohmiya

### **Break**

### **Invited Lecture III**

17:15-17:40      IL-13: Yi-Hsin Liu

17:40-18:05      IL-14: Teruyuki Nakato

18:05-18:30      IL-15: Fa-Kuen Shieh

**Banquet: 19:00-**

**[18 Dec., 2016]**

### **Invited Lecture IV**

10:00-10:25      IL-16: Kevin C. W. Wu

10:25-10:50      IL-17: Tatsuo Kimura

10:50-11:15      IL-18: Kuo-Chuan Ho

11:15-11:40      IL-19: Nobuyoshi Miyamoto

**11:40-**            **Closing Remark**            Kevin C. W. Wu

## **(IL-1) An energetics descriptor for designed synthesis of microporous framework materials: A case of aluminosilicate zeolites**

*Watcharop Chaikittisilp\**, Koki Muraoka, and Tatsuya Okubo

*The University of Tokyo, Tokyo 113-8656, Japan*

*E-mail: [watcha@chemsys.t.u-tokyo.ac.jp](mailto:watcha@chemsys.t.u-tokyo.ac.jp)*

Linking the energetics clues to the formation pathways of microporous framework materials is of great scientific and technological significance as it can provide a critical basis for materials design. Zeolite is a class of crystalline microporous silica-based framework materials that has been utilized in various fields across chemical industries.<sup>[1]</sup> The frameworks structures of zeolites are constructed from corner-sharing, tetrahedrally-coordinated  $TO_{4/2}$  primary units (where T is a tetrahedral atom such as Si, Al, B, Zn, etc.). When Si at the tetrahedral site (T site) of the zeolite frameworks is substituted by di- or trivalent atoms, negative charges at oxygen surrounding the substituting atoms are generated, thereby yielding anionic silicate-based frameworks. These negative tetrahedra require cationic charge-compensators that are typically active species for adsorption and catalysis. The contents and locations of substitutes are, therefore, one of the key factors determining the physicochemical properties of zeolites. Systematic evaluation of the characteristics of zeolites with a wide variety of framework topologies, a wide range of substituting contents, and various locations of substitutes is of great significance, but very challenging due to the limited ranges of the realizable chemical compositions in the existing zeolites as well as the limitation of the current analytical techniques.

Here, we present the systematic computational evaluation of the energetics of aluminosilicate zeolites with comprehensive ranges of framework structures, substituting contents, and atomic distributions.<sup>[2]</sup> The results coincide well with the structural knowledge obtained experimentally. The relation between the relative framework energies versus the substituting contents varies in accordance with the framework structures, suggesting that the relative thermodynamic stability of zeolites depends not only on the framework structures themselves, but also on the contents and locations of Al. The energetics of aluminosilicate zeolites can be considered as a design descriptor that reflects the framework stabilization required for the synthesis of zeolites.

**References:** [1] M. E. Davis, *Chem. Mater.* **2014**, *26*, 239–245. [2] K. Muraoka, W. Chaikittisilp and T. Okubo, *J. Am. Chem. Soc.* **2016**, *138*, 6184–6193.

## **(IL-2) Design and development of near-infrared mechanoluminescent materials as a new class of nanoprobe for in vivo imaging.**

*Sunao Kamimura<sup>1,2\*</sup>*

<sup>1</sup>*Kyushu institute of technology, Japan*

<sup>2</sup>*JST-PRESTO, Japan*

*E-mail: kamimura-sunao@che.kyutech.ac.jp*

Luminescence is usually generated when a material is excited using an external light source of appropriate, such as an electron beam, UV or visible light or X-rays. We also note a special class of materials that exhibit luminescence in response to the application of a mechanical stimulus, mechanoluminescence (ML); ML material is of particular interest for use in stress sensing devices which detect damage, fracture, and deformation in various structures. More recently, I have succeeded in developing a new ML material that emits near-infrared (NIR) light. This NIR ML occurs within the conventional optical window (650-950nm) for biological imaging and extends to 1400 nm, the second and arguably a more attractive optical window for in vivo imaging. In this lecture, I would like to introduce a design and development of ML material. Moreover, in a simple proof of practice demonstration, I'd like to propose the usefulness of NIR ML material as a new class of fluorescent nanoprobe for in vivo imaging for visualizing real-time forces in living tissue.

### **(IL-3) Mesoporous metal-organic frameworks with Kagomé topology**

*Kulandai vel sivasankar, Sheng-Han Lo, Duraisamy Senthil Raja, and Chia-Her Lin\**

*Chung-Yuan Christian University, Taiwan*

*E-mail: chiaher@cycu.edu.tw*

A mesoporous metal-organic framework of  $[Al(OH)(PDA)]$  (AIPDA; PDA = 4,4'-[1,4-phenylenebis(ethyne-2,1-diyl)]-dibenzoate anion) was synthesized by using Al(III) ions and  $H_2PDA$  under conventional reflux reactions. CYCU-10 has core 1D inorganic chains forms by corner-sharing octahedral  $AlO_6$  and further connected by the carboxylate ligands to form the Kagomé topology. These inorganic chains are linked together by the PDA ligands to generate two types of 1D channels of hexagonal mesopores and triangular micropores. As verified by  $N_2$  sorption measurements at 77 K, CYCU-10 showed Type I with secondary uptakes isotherms which reveal of both microporous and mesoporous materials. The analysis from the data gave a Brunauer-Emmett-Teller (BET) surface area of  $2635\text{ m}^2/\text{g}$  and pore volume of  $2.2\text{ cm}^3\text{ g}^{-1}$ . The pore size distribution derived from the  $N_2$  adsorption isotherms using the density function method suggests pore sizes of approximately 1.9 and 4.1 nm. In addition, the study on the relation between preparation and adsorption properties also displayed.

### **(IL-4) Stimuli-responsive materials consisting of cylindrical clay mineral "imogolite"**

*Kazuhiro Shikinaka\**

*Tokyo University of Agriculture and Technology, Japan*

*E-mail: k-shiki@cc.tuat.ac.jp*

Imogolite (IG) is a single-walled alumino-silicate type rigid cylindrical clay mineral with the formula of  $(HO)_3Al_2O_3SiOH$  and a well-defined size. The external and internal diameters are approximately 2 and 1 nm,

respectively. In contrast, their length ranges from several ten-nanometres to several micrometres. The outer and inner surfaces of IG are covered with aluminol and silanol groups, respectively, where protonation–deprotonation equilibria such as [outer surface]  $\text{Al}(\text{OH})_2 + \text{H}^+ \rightleftharpoons \text{Al}(\text{OH})\text{O} + \text{H}_2$  and [inner surface]  $\text{Si}-\text{OH} \rightleftharpoons \text{Si}-\text{O}^- + \text{H}^+$  occur. Because of these protonation–deprotonation behaviors, the dispersibility of IG in water strongly depends on the pH and ionic strength. That is, when dissolved in neutral to acidic and relatively low-ionic strength aqueous media, IG gives transparent or opaque solutions containing mono-disperse nanotubes or thin bundles. Recently, we created stimuli-responsive hydrogels consisting of IG and dicarboxylic acids that exhibit thixotropy, reversible solid/liquid transition behavior in response to mechanical shocks. Furthermore, after flow-orienting and subsequent standing the liquid-state mixture, the uniaxial alignments of IG nanofibers with centimeter scale were realized in the recovered gel. The self-standing interpenetrated network gels with the desired shapes were prepared by the in-situ polymerization of the uniaxially oriented gels that were pre-impregnated by 2-hydroxyethyl acrylate and a cross-linker. The confinement of the IG nanofibers with the uniaxial orientation induced some anisotropic physical properties to the gels such as anisotropic proton conductivity and mechanical strength. The specific abilities of the IG thixotropic gel, such as macroscopic supramolecular chiral ordering of the IG nanotubes via combination with chiral DAs, also indicate significant potential for the use of the thixotropic gel as chiral sensing materials, multi-stimuli-responsive actuators, etc.

#### **(IL-5) Self-assembly of polymer-brush-decorated particles synthesized by surface-initiated living radical polymerization**

*Kohji Ohno\**

*Kyoto University, Japan*

*PRESTO, JST*

*E-mail: [ohno@scl.kyoto-u.ac.jp](mailto:ohno@scl.kyoto-u.ac.jp)*

Synthesis and self-assembly of fine particles grafted with well-defined polymer brushes are described. Monodisperse silica particles (SiPs) of diameter between 100 and 1500 nm were surface-modified in a mixture of ethanol/water/ammonia with a newly designed triethoxysilane having an atom transfer radical polymerization (ATRP) initiating site, (2-bromo-2-methyl)propionyloxyhexyl triethoxysilane. The surface-initiated ATRP of methyl methacrylate (MMA) mediated by a copper complex was carried out with the initiator-fixed SiPs in the presence of a “sacrificial” (free) initiator. The polymerization proceeded in a living manner in all examined cases, producing SiPs coated with well-defined PMMA of a target molecular weight up to 480 k with a graft density as high as 0.7 chains/nm<sup>2</sup>. These PMMA-SiP hybrid particles had an exceptionally good dispersibility in organic solvents.

A colloidal crystal was newly identified for a liquid suspension of the PMMA-SiP hybrid particles. With increasing particle concentration, the suspension progressed from a (disordered) fluid to a fully

crystallized system, going through a narrow crystal/fluid coexisting regime. The crystal had a face-centered-cubic structure with a surprisingly large nearest-neighbor interparticle distance, suggesting that the graft chains, highly extended due to the “concentrated brush effect”, exerted a long-range steric interaction. The crystalline structure was of closed-packed type in all cases, and the nearest-neighbor interparticle distance in the crystal increased with increasing graft chain length.

## **(IL-6) Functional Mesoporous Materials Templated by Block Copolymers**

*Shiao-Wei Kuo\**

*National Sun Yat-Sen University, Taiwan*

*E-mail: [kuosw19760501@gmail.com](mailto:kuosw19760501@gmail.com)*

Recently, we have utilized several unique amphiphilic block copolymers as templates, such as PE-PEO, PEO-PCL, PE-PEO-PCL, and PEO-PCL-PLLA to successfully fabricate a series of mesoporous materials, for example, mesoporous silicas, mesoporous phenolic resins and mesoporous carbons by a convenient EISA method. Firstly, we took PE-PEO as model block copolymer to study the TEOS-to-template or HCl-to-template weight ratio effect during the EISA process, view from the thermal dynamic point and kinetic reason, respectively. In addition, we expended the research method to the other block copolymer systems, especially for the unusual ABC type triblock copolymers, we obtained the hierarchical mesostructure by single template. These specific mesostructures could be observed easily by small angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and isotherm N<sub>2</sub> experiment. Moreover, blending technique could also be used in the templating process during EISA, the clear method could easily control the morphology and pore size of the mesoporous materials.

**Reference:** [1] Li, J. G.; Kuo, S. W. *Macromolecules* **2011**, *44*, 9295-9309. [2] Li, J. G.; Lin, R. B.; Kuo, S. W. *Macromol. Rapid Commun.* **2012**, *33*, 678-682. [3] Li, J. G.; Chuang, C. Y.; Kuo, S. W. *J. Mater. Chem.* **2012**, *22*, 18583-18595. [4] Li, J. G.; Jeng, U. S.; Kuo, S. W. *Macromol. Chem. Phys.* **2013**, *214*, 2115-2123. [5] Liu, C. C.; Li, J. G.; Kuo, S. W. *Macromolecules* **2014**, *47*, 6389-6400. [6] Lu, Y. S.; Bastakoti, B. P.; Pramanik, M.; Yamauchi, Y.; Kuo, S. W. *Chem. Eur. J.* **2016**, *22*, 1159-1164.

## **(IL-7) In-situ crystallization of layered silicates on amorphous silica**

*Tomohiko Okada\**

*Shinshu University, Japan*

*E-mail: [tomohiko@shinshu-u.ac.jp](mailto:tomohiko@shinshu-u.ac.jp)*

The fine crystals of a smectite-like layered silicate, whose negative layer charge is generated by an isomorphous substitution in the tetrahedral SiO<sub>4</sub> or octahedral MgO<sub>6</sub> framework, have grown on amorphous silica (monodisperse microspheres<sup>[1]</sup>, microfibers<sup>[2]</sup>, hollow microcapsules<sup>[3]</sup>, etc.). The fine, plate-like crystals were observed to thoroughly cover the surface of the silica substrate, irrespective of

their size and morphology, by the hydrothermal reactions of the silica substrate in aqueous alkali solution containing another elements (e.g., Al, Mg, and Li ions). Partial dissolution of the original silica substrate was required to initiate such crystallization, resulting in preserving the silica morphology. The layered silicates displayed cation-exchange reactions to expand the interlayer space, where they are often observed in a smectite system, but exfoliation (or osmotic swelling) did not occur in an aqueous LiCl solution. The firm immobilization of the layered silicates would be advantageous to a flow system application as filtering<sup>2</sup> and a HPLC column packing materials (optical resolution)<sup>[4]</sup>.

**Reference:** [1] T. Okada et al., *J. Phys. Chem. C*, **116**, 21864 (2012); *Microporous Mesoporous Mater.*, **215**, 168 (2015); *Clay Sci.*, **19**, 45 (2015); *Langmuir*, **31**, 13842 (2015). [2] T. Okada et al., *RSC Adv.*, **6**, 26130 (2016). [3] T. Okada et al., *Appl. Clay Sci.*, **132-133**, 320 (2016). [4] T. Okada et al., *J. Chromatogr. Sci.*, **54**, 1238 (2016).

### **(IL-8) Development of organic/inorganic hybrid materials by using a biomineralization-inspired method**

Tatsuya Nishimura\*

*Kanazawa University, Japan*

*E-mail: [nishimura@se.kanazawa-u.ac.jp](mailto:nishimura@se.kanazawa-u.ac.jp)*

Biomaterials such as bones, teeth, and seashell nacre are organic/inorganic hybrids with highly controlled hierarchical structures. These structures are formed under gentle conditions through self-organization processes that are controlled by macromolecular templates. Therefore, biomineralization-inspired crystallization of inorganic compounds with organic polymer templates is of great interest for the development of functional materials by an environmentally friendly way. In accordance with this idea, we previously reported the formation of thin films of inorganic crystals using a biomineralization approach.<sup>[1]</sup> The resulting hybrid materials consisting of inorganic crystals and organic polymers exhibited a wide variety of morphologies. Here we discuss our recent strategies for the development of new inorganic/organic hybrid materials such as structural materials with hierarchical order through self-organization process of the liquid crystals,<sup>[2]</sup> and the development of ZnO thin-film photocatalysts through a biomineralization-inspired method.<sup>[3]</sup> The use of poly(acrylic acid) contributed to the formation of amorphous precursors of these minerals in the aqueous solution, which was essential for inorganic crystallization on the polymer matrices.

**References:** [1] T. Nishimura, *Polym. J.* 2015, **47**, 235–243. [2] S. Matsumura, S. Kajiyama, T. Nishimura, T. Kato, *Small*, 2015, **11**, 5127-5133. [3] S. Matsumura, Y. Horiguchi, T. Nishimura, H. Sakai, T. Kato, *Chem. Eur. J.*, 2016, **22**, 7094-7101.

### **(IL-9) De novo synthesis of MOF derived, Cu doped mesoporous TiO<sub>2</sub> nanoparticles (Cu-MTNs) as an efficient photocatalyst for hydrogen production from water splitting**

Yu-Te Liao,<sup>1,2</sup> Yusuke Yamauchi,<sup>2,3</sup> Yusuke Ide<sup>2\*</sup> and Kevin C.-W. Wu<sup>1\*</sup>

<sup>1</sup>National Taiwan University, Taipei, Taiwan

<sup>2</sup>National Institute for Materials Science (NIMS), Japan

<sup>3</sup>University of Wollongong, Australia

E-mail: [Ide.Yusuke@nims.go.jp](mailto:Ide.Yusuke@nims.go.jp); [kevinwu@ntu.edu.tw](mailto:kevinwu@ntu.edu.tw)

Titania is a well-known photocatalyst with high performance under UV-light. Since the photocatalytic efficiency of titania largely depends on the surface area and charge separation efficiency, tremendous effort has been focus on synthesizing better-performance titania materials in consideration of their morphology (size, porosity, and so on) and hybridization of co-catalyst like precious metals (to enhance the charge separation). *De novo* synthesis is a novel approach for synthesizing guest molecules-encapsulated, MOF-derived nanoporous materials. Different from *in situ* synthesis, the guest molecules are delivered into under-constructed framework via *de novo* approach. Some advantages of *de novo* synthesis, such as well distribution of guest molecules and size selection of framework, are considered as positive effect on catalysis.

In this work, we used a metal-organic framework, MIL-125, where titania is in the original framework and copper as the guest molecule. Copper ions were introduced into under-constructed MIL-125. The organic linker, BDC, chelated with Ti complex and Cu complex at the same time, forming MIL-125 with uniform distribution of Cu complex inside framework. Cu-loaded MIL-125 would become mesoporous TiO<sub>2</sub> nanoparticles (MTNs) with anatase phase after calcination. Hydrogen generation from water via photocatalysis was used to evaluate the performance of Cu-doped MTNs (Cu-MTNs). The results shows that commercial titania (P25) and MTNs have only low photocatalytic ability for the reaction. After doped with Cu through *de novo* approach, the photocatalytic ability further enhanced. We will discuss the mechanism of such high performance of Cu-MTNs.

## **(IL-10) Local thermal non-equilibrium in the core-shell nanospace induced by microwave irradiation**

Dai Mochizuki\*

Shinshu University, Japan

E-mail: [daim@shinshu-u.ac.jp](mailto:daim@shinshu-u.ac.jp)

Microwave irradiation often induces the enhancement of yields and reaction rates in chemical reaction. We have focused on the microwave thermal effect observed as local thermal non-equilibrium in heterogeneous catalytic reaction,<sup>[1-2]</sup> and synthesized a new type core-shell catalyst composed of Carbon-filled-Zeolite core and Zeolite shell.<sup>[3]</sup> Carbon is an excellent microwave susceptor compared to zeolite, thus this catalyst is anticipated to make differences in the temperature between the shell where the reaction occurs and the outside of catalyst under microwave irradiation, which leads to the enhancement of the reaction in the shell. We have investigated the rate enhancement in the

heterogeneous reaction.

Core-shell zeolite was determined by SEM and AES mapping of the cross section of one particle of the zeolite.

It shows a localization of carbon material in the core region. In the same reaction temperature, the enhancement in the reaction rate was observed under microwave irradiation compared to oil bath heating. There were no such enhancements when normal zeolite Y was used in the control experiment. This effect should be attributed to the local thermal non-equilibrium due to the selective heating of carbon in the core. The local thermal non-equilibrium was also confirmed by measuring the temperature of the surface of the core-shell structures.

**References:** [1] D. Mochizuki, M. Shitara, M. M. Maitani, Y. Wada, *Chem. Lett.* 1409 (2012). [2] Z. Chen, D. Mochizuki, M. M. Maitani, Y. Wada, *Nanotechnology* 265602 (2013). [3] D. Mochizuki, M. M. Maitani, Y. Wada, *J. Catal.* 1 (2015).

### **(IL-11) Spatiotemporal control of self-oscillating gel by uniformly aligned inorganic nano sheets**

*Youn Soo Kim,<sup>1\*</sup> Yasuhiro Ishida,<sup>2</sup> Yasuo Ebina,<sup>3</sup> Takayoshi Sasaki,<sup>3</sup> Ryo Yoshida,<sup>1</sup> and Takuzo Aida<sup>1,2</sup>*

<sup>1</sup>*The University of Tokyo, Japan*

<sup>2</sup>*RIKEN Center for Emergent Matter Science (CEMS), Japan*

<sup>3</sup>*National Institute for Materials Science (NIMS)*

*E-mail: [kim@cross.t.u-tokyo.ac.jp](mailto:kim@cross.t.u-tokyo.ac.jp)*

A novel “self-oscillating” gel that exhibits an autonomous mechanical swelling–deswelling oscillation without any on–off switching of external stimuli has been developed since 1996.<sup>[1]</sup> The basic chemical structure of the self-oscillating polymer is a copolymer of *N*-isopropylacrylamide (NIPAAm) and Ru(bpy)<sub>3</sub> as a catalyst for the Belousov–Zhabotinsky (BZ) reaction. In response to the redox change of Ru(bpy)<sub>3</sub> units, hydrophilicity and LCST of gel matrices change, which causes the swelling and deswelling of the gel networks. Unilamellar titania nanosheet (TiNS) is quite attractive, owing to its highly anisotropic shape and unique magnetic properties, where TiNSs in an aqueous dispersion magnetically align cofacially. Through in-situ polymerization, the aligned structure of TiNSs can be chemically locked in the hydrogel network.<sup>[2-4]</sup> Based on this strategy, we fabricated an anisotropic self-oscillating hydrogel by hybridization of polyNIPAAm and Ru(bpy)<sub>3</sub> units with uniformly aligned TiNSs. The as-prepared hydrogel showed autonomous swelling/deswelling behavior driven by BZ reaction, in a highly anisotropic manner.

**References:** [1] Yoshida, R.; Takahashi, T.; Yamaguchi, T.; Ichijo, H. *J. Am. Chem. Soc.* **1996**, *118*, 5134. [2] Liu, M.; Ishida, Y.; Ebina, Y.; Sasaki, T.; Aida, T. *Nat. Commun.* **2013**, *4*, 2029. [3] Liu, M.; Ishida, Y.; Ebina, Y.; Sasaki, T.; Hikima, T.; Takata, M.; Aida, T. *Nature* **2015**, *517*, 68. [4] Kim, Y.S.; Liu, M.; Ishida, Y.; Ebina, Y.; Osada, M.; Sasaki, T.; Hikima, T.; Takata, M.; Aida, T. *Nature Mat.* **2015**, *14*, 1002.

**(IL-12) Visible light-induced photocatalytic H<sub>2</sub>O<sub>2</sub> generation from O<sub>2</sub> saturated aqueous suspension of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> adsorbed mesoporous silica modified with phenyl sulfonic acid group**

*Minoru Sohmiya\**

*Waseda University, Japan*

*E-mail: [minoru.sohmiya@gmail.com](mailto:minoru.sohmiya@gmail.com)*

H<sub>2</sub>O<sub>2</sub> has been considered as an energy carrier for fuel cells offering an alternative to H<sub>2</sub> or methanol because H<sub>2</sub>O<sub>2</sub> is soluble in water and can be used in an one-compartment fuel cell which does not require the separator. H<sub>2</sub>O<sub>2</sub> is produced industrially by the energy-consuming anthraquinone method. Thus, photocatalytic H<sub>2</sub>O<sub>2</sub> production attracts attention and has been investigated using semiconductors such as TiO<sub>2</sub>. The reactions have been carried out, generally, by UV irradiation in O<sub>2</sub> saturated aqueous solution with an electron and proton donor (sacrificial reagent), like alcohols. Photoactive molecules such as metal complexes have been also studied as the visible-light-responsive photocatalysts. It was reported that [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, which is a well-known complex showing photoinduced redox potential, produced H<sub>2</sub>O<sub>2</sub> photocatalytically in solution, though the reaction required sacrificial reagent. In this study, we find that the incorporation of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> into the pore of mesoporous silica modified with sulfonated phenyl group enables the photocatalytic H<sub>2</sub>O<sub>2</sub> generation without sacrificial reagent. In addition, the photocatalytically produced H<sub>2</sub>O<sub>2</sub> works as the oxidant by photo-Fenton reaction for the sequential reaction, organic molecules oxidation, with high selectivity.

**(IL-13) Highly-ordered on-substrate mesoporous zeolitic ultrathin films with controlled shapes**

*Yi-Hsin Liu\*<sup>1</sup> and Chung-Yuan Mou<sup>2</sup>*

*<sup>1</sup>National Taiwan Normal University, Taiwan*

*<sup>2</sup>National Taiwan University, Taiwan*

*E-mail: [yliu@ntnu.edu.tw](mailto:yliu@ntnu.edu.tw)*

Structure directing agents (SDAs) provide practical intermolecular interactions, not only served as soft-templates to guide formation of mesostructures but also utilized as bridging ligands that assist transformation of pre-crystalline precursors into solid phases. Highly-ordered on-substrate mesoporous zeolitic ultrathin films (MZUFs) were rationally synthesized in a mixture of ternary SDAs, containing C<sub>16</sub>TAB, SDS and decane in Stöber-like solution. The ultrathin films (~20 nm) were deposited via deliberately introduction of beta-zeolite seeds at 40-50°C, resulting formation of highly uniform hexagonal packing of mesochannels with controlled shapes and well-defined pore sizes (5-8 nm). The zeolite films were further examined in both top-view and cross-sectional SEM/HRSEM/TEM and GISAXS techniques which confirmed such an unusual bi-layer structure having Moiré and corresponding superlattice patterns. Upon calcination, the 3D hexagonal thin films gradually transformed into 2D hexagonal ones with single-layer vertical

thickness (~5 nm) and resolved in-plane diffraction patterns, mechanistically similarly to crystalline titania and alumina thin film materials.

#### **(IL-14) Phase-separated structure of colloidal liquid crystalline binary inorganic nanosheets**

Teruyuki Nakato\*

*Kyushu Institute of Technology, Japan*

*E-mail: [nakato@che.kyutech.ac.jp](mailto:nakato@che.kyutech.ac.jp)*

Inorganic layered materials can be converted to colloidal liquid crystals (LCs) through exfoliation into inorganic nanosheets. Among nanosheet LCs, binary nanosheet systems are interesting because of their rich structures based on phase-separation of the two nanosheet species. We have developed a binary system of niobate ( $K_4Nb_6O_{17}$ ) and smectite-type clay nanosheets. Although this system is apparently homogeneous at a macroscopic scale, small-angle X-ray scattering measurements indicate the niobate nanosheets form a lamellar LC phase, which is separated from an isotropic phase of clay nanosheets. The LC phase is compressed by the coexisting isotropic phase, as evidenced by shrinkage of the basal spacing of the lamellar structure. Variation in the lateral size of clay nanosheets (from several tens of nanometers to a few micrometers) does not affect the basal spacing of the phase separated LC phase. Such a phase-separated structure is visualized in a real space by confocal laser scanning microscopy (CLSM). CLSM images of scattered light reflect the location of the niobate nanosheets while those of fluorescence can monitor the location of clay nanosheets adsorbed by a cationic dye. CLSM observations clarify that the niobate nanosheets form domains with the size of several tens of micrometers and the domains are located in a lamellar manner. Some voids are observed between the niobate domains, and the voids are occupied by the clay nanosheets.

#### **(IL-15) Spatial Confinement Effect in Metal-organic Frameworks Conquers Enzyme Unfolding: Enhanced Biological Stability of Catalase@ZIF-90 in Urea**

*Fu-Siang Liao<sup>1</sup>, Wei-Shang Lo<sup>1</sup>, Chang-Cheng Wu<sup>1</sup>, Yu-Shen Hsu<sup>1</sup>, Shao-Chun Wang<sup>1</sup>, Fa-Kuen Shieh\*<sup>1</sup>, Yusuke Yamauchi<sup>2</sup>, Tzu-Yen Huang<sup>3</sup>, Kevin C.-W. Wu<sup>3</sup>, and Chia-Kuang Tsung<sup>4</sup>*

*<sup>1</sup>National Central University, Taiwan; <sup>2</sup>National Institute for Materials Science (NIMS), Japan; <sup>3</sup>National Taiwan University, Taiwan; <sup>4</sup>Boston College, United States*

*E-mail: [fshieh@cc.ncu.edu.tw](mailto:fshieh@cc.ncu.edu.tw)*

We demonstrate a spatial confinement of enzyme in metal-organic frameworks (MOFs) to prevent enzyme unfolding from denaturing agents, resulting in enhanced biochemical stability for immobilized enzyme. A hydrogen peroxidase, catalase, was confined in a limited space within the structure of Zeolitic Imidazolate Frameworks (ZIFs), a subgroup of MOFs, through a de novo synthesis (namely, catalase@ZIF-90). Because of limited space, the immobilized catalase cannot unfold into its denatured conformation even with the

presence of the denaturing reagent (i.e. urea). For example, with 8 M urea, the results of catalytic assays showed that CAT@ZIF-90 retained the biological function of  $k_{\text{obs}} \approx 3 \times 10^{-4} \text{ s}^{-1}$  while free catalase showed undetectable activity. In contrast to spatial confinement provided by ZIF-90, the conventional encapsulation of catalase in mesoporous materials (i.e., SBA-15 and MCF) by physical adsorption did not show any protection from enzyme unfolding. Our new spatial confinement of enzyme in ZIF-90 structure could prevent conformational change of enzyme from denaturing agents, thus enhance the corresponding biochemical stability, which would expand the possibility of immobilized enzyme in practical applications.

### **(IL-16) Metal-organic frameworks (MOFs)-derived catalysts for an effective HMF-to-FDCA and HMF-to-DMF conversions**

Kevin C.-W. Wu\*

*National Taiwan University, Taiwan*

*E-mail: [kevinwu@ntu.edu.tw](mailto:kevinwu@ntu.edu.tw)*

Metal-organic frameworks (MOF) consist of organic molecular linkers bonded to metal-based nodes. MOFs have advantages such as tunable porosity, chemical stability, ultra-high specific surface area and ability to tune the surface chemistry. These features have enabled MOFs to find applications in diverse research fields, especially in heterogeneous catalysis. In this presentation, we will use MOFs-derived nanoporous nanoparticles as effective solid catalysts for converting 5-hydroxymethylfurfural (HMF), one of the most promising platform of lignocellulosic biomass, into dimethylfuran (DMF) and 2,5-furandicarboxylic acid (FDCA) through hydrogenation/hydrogenolysis and oxidation, respectively. The results obtained in this study indicated that high yields of DMF and FDCA could be separately obtained from HMF via the combination of our newly designed MOFs-based nanoporous catalysts with the liquid-phase hydrogen/oxygen sources.

**References:** [1] Green Chemistry. 2016, DOI: 10.1039/C6GC02118B. [2] Journal of the American Chemical Society. 2015, 137, 4276-4279. [3] ChemSusChem. 2015, 8, 789-794. [4] ChemSusChem. 2014, 7, 3421-3426.

### **(IL-17) Porous materials design based on framework shrinkage as the great potential to obtain unique and high-surface-area films**

Tatsuo Kimura\*

*National Institute of Advanced Industrial Science and Technology (AIST), Japan*

*E-mail: [t-kimura@aist.go.jp](mailto:t-kimura@aist.go.jp)*

Supramolecular assisted synthesis of inorganic oxides is conceptually very attractive and actually useful for obtaining a wide variety of highly ordered mesoporous materials, which have also applied to their morphological and compositional designs. Recently I have reviewed morphologically controlled mesoporous materials synthesized using assemblies/aggregates of amphiphilic organic

molecules/copolymers and thus reached to significant closing remarks through fruitful discussions with top-level scientists who are core members as a series of this joint workshop (see following review articles; T. Kimura\*, *Chem. Rec.*, **2016**, *16*, 445; S. Dutta, K. C.-W. Wu\*, T. Kimura\*, *Chem. Mater.*, **2015**, *27*, 6918; B. P. Bastakoti, Y. Li, T. Kimura, Y. Yamauchi\*, *Small*, **2015**, *11*, 1992. ). From the viewpoint, I would like to introduce the main contents of three review articles in this workshop but especially focus on the porous materials design based on framework shrinkage. Considering inorganic/organic interfaces in multiscale between inorganic oxide and organic fractions (e.g., frameworks, self-assembled nanostructures, confined macrospace), several framework shrinkages are predictable and explained by using simple illustrations, being advantageous for porous materials design to imaging resultant materials having unique nanostructures and high surface area.

### **(IL-18) Amperometric Detection of Nitrite Based on the Thin Film of MOF-525/Graphene Nanoribbons**

*Kuo-Chuan Ho\**, and *Chung-Wei Kung*

*National Taiwan University, Taiwan*

*E-mail: [kcho@ntu.edu.tw](mailto:kcho@ntu.edu.tw)*

Graphene nanoribbons (GNRs) are incorporated with the nanocrystals of a porphyrinic metal-organic framework, MOF-525, by solvothermally growing MOF-525 in the suspension of well-dispersed GNRs. The nanocomposite, which is composed of the MOF-525 nanocrystals interconnected by numerous one-dimensional GNRs, is successfully synthesized. Due to the excellent dispersity, uniform thin films of the MOF-525/GNRs nanocomposite can be simply deposited on conducting glass substrates by using drop casting. The obtained thin film of MOF-525/GNRs nanocomposite is applied for electrochemical nitrite sensor. The MOF-525 nanocrystals are served as a high-surface-area electrocatalyst toward nitrite and the interconnected GNRs act as conductive bridges to render facile charge transport. The thin film of MOF-525/GNRs nanocomposite thus exhibits a much better electrocatalytic activity for the oxidation of nitrite compared to the pristine MOF-525 thin film.

### **(IL-19) Liquid crystal phase of inorganic nanosheet colloids and their applications**

*Nobuyoshi Miyamoto\**

*Fukuoka Institute of Technology, Japan.*

*E-mail: [miyamoto@fit.ac.jp](mailto:miyamoto@fit.ac.jp)*

Liquid crystal (LC) phase of inorganic nanosheet is fascinating system for potential applications in many fields.<sup>[1-5]</sup> In this lecture, I present my researches on LC nanosheet colloids and their applications. Structural analyses by small angle X-ray scattering<sup>[6]</sup> and confocal laser scanning microscopy reveals not only meso-scale lamellar or nematic structures in the LC phase but also fractal-like porous structures. In that structure, the nanosheets show translational and rotational Brownian motions as revealed by fast-scanning

confocal laser microscopy. The structure is tunable by many factors such as nanosheet concentration, nanosheet lateral size, salt concentration, solvent, counter cations, and charge density of the nanosheets. Some optimized systems show variable structural colors which will be useful for color materials and sensor devices. Under ac-electric field, the orientation of the nanosheets and LC domain is easily controllable; the electric field response is applicable for fabrication of electro-optic devices and formation of anisotropic composite materials. Among many future applications, inorganic nanosheet/polymer composites with precisely controllable hierarchical structure are fascinating. We synthesized a cm-scale mono-domain gel of exfoliated LC clay/polymer composite.<sup>[7]</sup> The gel is *printable* with a dye and the colored part shows photo-induced anomalous deformation behavior, which will be suitable as soft actuators.

**References:** [1] Miyamoto, N.; Nakato, T. *Israel J. Chem.* **2012**, *52*, 881. (a review paper). [2] Miyamoto, N.; Nakato, T. *Adv. Mater.* **2002**, *14*, 1267. [3] Miyamoto, N.; Iijima, H.; Ohkubo, H.; Yamauchi, Y. *Chem. Commun.* **2010**, *46*, 4166. [4] Guégan, R.; Sueyoshi, K.; Anraku, S.; Yamamoto, S.; Miyamoto, N., *Chem. Commun.* **2016**, *52*, 1594 – 1597. [5] Miyamoto, N.; Yamamoto, S.; Shimasaki, K.; Harada, K.; Yamauchi, Y., *Chem. Asian J.* **2011**, *6*, 2936-2939. [6] Yamaguchi, D.; Miyamoto, N.; Fujita, T.; Nakato, T.; Koizumi, S.; Ohta, N.; Yagi, N.; Hashimoto, T. *Phys. Rev. E.* **2012**, *85*, 011403. [7] N. Miyamoto, M. Shintate, S. Ikeda, Y. Hoshida, Y. Yamauchi, et al. *Chem. Commun.* **2013**, *49*, 1082; Inadomi, T.; Ikeda, S.; Okumura, Y.; Kikuchi, H.; Miyamoto, N. *Macromol. Rapid Commun.* **2014**, *35*, 1741.