KYOTO UNIVERSITY
Global COE Program
INTEGRATED
MATERIALS SCIENCE

7th Symposium on Soft Chemistry toward Functional Materials

グローバルCOE シンポジウム「低温合成法による新機能性材料の創製（第７回）」

(*Kyoto University Global COE Program "Integrated Materials Science”*)
Date: March 4, 2009
Place: Katsura Campus Room A2-303 (Kyoto University, Japan)

10:35 Opening Remarks: Hiroshi Kageyama (Graduate School of Science, Kyoto University)

[Chair] Takeshi Abe (Graduate School of Engineering, Kyoto University)

10:40 “Functional Self Assembled Monolayers: Assembly of Donor – Spacer –Acceptor Molecules on Gold Surfaces”
Srinivasan Sampath (Department of Inorganic and Physical Chemistry, Indian Institute of Science, India)

11:40 “Mono-molecular Layers Covalently Bonded to Silicon Formed through a Photochemical Reaction at Room Temperatures”
Hikaru Sano (Graduate School of Engineering, Kyoto University)

(12:00 - 13:30 Lunch)

[Chair] Kazuyoshi Kanamori (Graduate School of Science, Kyoto University)

13:30 “Function-integrated Hybrid Materials Fabricated via the Molecular Assembly Technique”
Kiyofumi Katagiri (Graduate School of Engineering, Nagoya University)

14:20 “Fabrication of Hybridized Porous Coordination Framework Crystals”
Shuhei Furukawa (Institute for Integrated Cell-Material Sciences, Kyoto University; ERATO Kitagawa Integrated Pores Project, JST)

(15:10 - 15:30 Coffee Break)

[Chair] Hiroshi Kageyama (Graduate School of Science, Kyoto University)

15:30 “Low Temperature Topochemical Methods for the Construction of Metal-Anion Layers within Receptive Perovskite Hosts”
John B. Wiley (Department of Chemistry, University of New Orleans, USA)

16:30 “Inorganic-Organic Hybrids Based on Layered Compounds: Preparation and Application”
Yoshiyuki Sugahara (Faculty of Science and Engineering, Waseda University)

17:20 Closing Remarks: Takeshi Abe (Graduate School of Engineering, Kyoto University)

Functional Self-Assembled Monolayers: Assembly of Donor - Spacer - Acceptor Molecules on Gold Surfaces

Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore, India

S Sampath

Chemical modification of surfaces has been a major area of research in interfacial electrochemistry. As part of our on-going research program, we have been involved in understanding the interfacial properties of modified surfaces / new materials and liquid / solid electrolytes. The materials that we are presently interested in, are self-assembled monolayers / LB film modified surfaces, exfoliated graphite / graphene oxide, nanobimetallic particles, and molten electrolytes.

The present talk will highlight some of our research work on organic thin films on conducting surfaces with special emphasis on

(a) assembly of donor - s spacer - acceptor molecules for molecular rectification and intra / intermolecular electron transfer;
(b) assembly of zein protein on surfaces of controlled wettability and its orientation
(c) understanding water structure near a hydrophobic surface and
(d) orientation dependent catalysis.

Some of our research work in the areas of SAMs and briefly, the assembly of graphene oxide will be discussed in the present lecture.

Mono-molecular Layers Covalently Bonded to Silicon Formed through a Photochemical Reaction at Room Temperatures

Hikaru Sano

Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan
hikarusano@t01.mbox.media.kyoto-u.ac.jp

Background: Unsaturated hydrocarbons such as 1-alkene are known to react with a hydrogen-terminated silicon (Si) through a thermal or UV light excitation, resulting in the formation of a self-assembled monolayer (SAM) directly attached to the Si surface without an intermediate oxide layer (Figure 1). Besides thermal and UV light excitation processes, a process utilizing visible light has been reported.[1] This method may cause less damage to organic molecules so that this process is more attractive. Nevertheless, the visible light excitation process for SAM formation has not been elucidated in detail. In the present study, we have investigated the SAM formation behavior from 1-hexadecene on hydrogen-terminated Si(111) (H-Si(111)) surfaces under irradiation with visible light at room temperature.

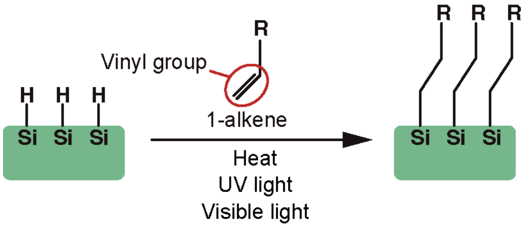


Figure 1. Unsaturated hydrocarbons such as 1-alkene are known to react with hydrogen-terminated silicon surface through thermal or photo excitation of the substrate.

Experimental: A H-Si(111) sample surface immersed in neat 1-hexadecene liquid was irradiated with a Xe lamp through a band-pass filter (300 nm, 400 nm, 550 nm, 700 nm, FWHM ≈ 10 nm) for 2 – 32 hours at room temperature. Chemical and physical properties of the resulting samples were characterized by water contact angle measurements, X-ray photoelectron spectroscopy (XPS), ellipsometry, and atomic force microscopy (AFM).

Results and discussion: Results of water contact angles, carbon contents obtained from XPS quantitative analysis and ellipsometric thicknesses of each sample indicate that the irradiated light with each wavelength certainly promoted the SAM formation and that the reaction rate become faster as the irradiation wavelength shortened. Most importantly AFM images obtained on the SAM-covered samples have similar topographic images to that on H-Si(111) with terraces and mono-atomic steps, indicating that mono-molecular layers with high uniformity are formed on the H-Si(111) surface (Figure 2). Since UV/Vis spectroscopy showed that 1-hexadecene molecules do not absorb light with wavelengths between 300 and 800 nm, the irradiated light was considered to excite the Si substrate itself. In addition, the optical absorption coefficient of single crystal Si at 300 nm is about 770 times larger than that at 700 nm. Therefore, the generation of a hole/electron pair with an excitation photon is plausible as rate controlling step of the whole reaction between H-Si(111) surface and 1-alkane.

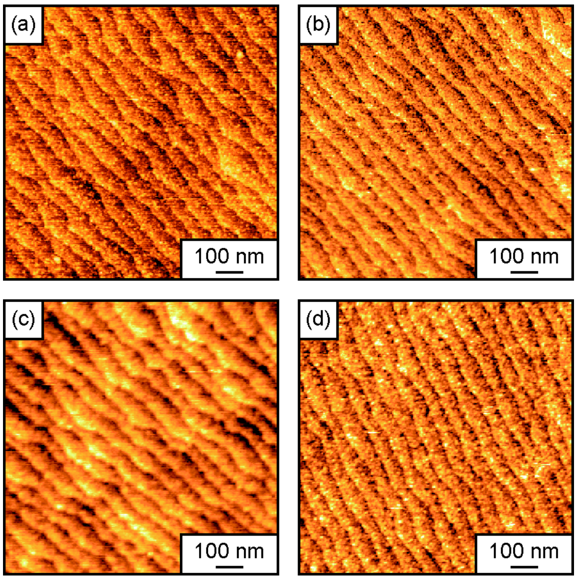


Figure 2. Topographic images of the samples (a) before and after irradiation with (b) 400, (c) 550 and (d) 700 nm in wavelength for 32 h.

References:

[1] Q. -Y. Sun, L. C. P. M. de Smet, B. van Lagen, M. Giesberts, P. C. Thuene, J. van Engelenburg, F. A. de Wolf, H. Zuilhof, and E. J. R. Sudhölter, *J. Am. Chem. Soc.*, **127**, 2514 (2005).

Function-integrated Hybrid Materials Fabricated
via the Molecular Assembly Technique

Kiyofumi Katagiri

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.

*E-mail: katagiri@apchem.nagoya-u.ac.jp

Researches on organic-inorganic hybrid materials have been continuously attracted much attention from the community of materials science. At the incunabulum stage, these materials were obtained by mixing inorganic precursors with organic polymers, using organically modified metal alkoxides, or doping functional molecules into the inorganic gels. However, it is not easy to control the nanostructure of hybrid materials by these techniques. In the past decade, a number of nanostructured materials have been developed with the evolution of supramolecular science. At the current stage, the technique of molecular assembly is an important strategy to control structure and functions of hybrid materials. Functions of organic and inorganic components are conjugated in these nanohybrids and novel properties generated by integration of their functions are expected. Here, the several approaches of function-integrated hybrid materials fabricated via the molecular assembly technique are introduced.

1) “Cerasome” as a lipid bilayer vesicle with siloxane surface

Lipid bilayer vesicles, known as liposomes, have been studied not only for cell membrane models also for drug carriers, and substrates of molecular devices. However, the morphology of liposome is not stable since it forms by weak molecular interaction. In 1999, “cerasome” was developed by sol-gel reaction and self-assembly of organoalkoxysilanes which have analogous structure with bilayer forming lipids [1]. The cerasomes have high morphological stability compared to conventional liposomes due to their inorganic frameworks on the surface. Furthermore, the hierarchically multicellar assembly of cerasomes on the substrate was achieved by layer-by-layer assembly of oppositely charged cerasomes [2].

2) External stimuli responsive hybrid hollow capsules prepared via layer-by-layer assembly

One of the most suitable methods to fabricate microcapsules is the layer-by-layer (LbL) assembly technique [3]. The process consists of the successive deposition of oppositely charged polyelectrolytes on colloidal particles, followed by removal of the core. Now a number of efforts are devoted for the development of “smart capsules” with stimuli-responsive behavior. We have developed stimuli-responsive hybrid microcapsules, comprising polyelectrolyte multilayers coated with lipid bilayers and metal oxides, such as TiO_2 and Fe_3O_4, via the LbL colloid-templating technique and the solution process for inorganic materials synthesis. The encapsulated molecules can be released on demand by the external field irradiation due to the changes of molecular permeability of hollow shells [4].

[1] (a) K. Katagiri *et al*., *Chem. Lett*., 661 (1999). (b) K. Katagiri *et al*., *Chem. Eur. J*., **13,** 5272-5281 (2007).

[2] K. Katagiri *et al*., *J. Am. Chem. Soc*., **124**, 7892 (2002).

[3] K. Katagiri *et al*., *Soft Matter*, **2,** 18-23 (2006).

[4] K. Katagiri *et al*., *Chem. Mater*., **21,** 195-197 (2009).

Fabrication of Hybridized Porous Coordination Framework Crystals

Shuhei Furukawa

ERATO Kitagawa Integrated Pores Project, JST & Institute for Integrated Cell-Material Sciences, Kyoto University

Well-designed metal–organic hybrid porous materials—so-called porous coordination polymers (PCPs) or metal–organic frameworks (MOFs)—can be made from an assembly of organic linkers with metal ions. This class of materials was recently recognized as an intriguing class of crystalline nanoporous materials for gas sorption, separation, and catalysis because their framework topologies and pore sizes can be designed for selective guest accommodation, and the functionality of the pore surfaces directly influences the interaction with guest molecules.

Porous properties such as gas sorption and guest molecule accommodation should also correlate with the interfacial structure of porous materials because guest molecules (adsorbates) first encounter the surface of porous materials. Hence, the affinity of porous materials for guest molecules can be tuned by modifying the surface structure. There has been no report to directly modify the surface of PCP crystals, even though functionalization of PCP *outer* surfaces is a great challenge but a promising methodology not only for modification of the porous properties but also for the addition of a new function to the PCP without changing the characteristic features of the PCP crystal itself, resulting in the fabrication of multi-functional PCPs. Here we show the novel approaches to modify the surfaces of PCP crystals.

One way to decorate the crystal surfaces of a PCP is to hybridize the core PCP crystal with another shell crystal by epitaxial growth at a single crystal level, thus creating core/shell type PCP hetero-epitaxial crystals. Such a lattice match promises pore connections at the interface between crystals, where the modified crystal structure should influence the mobility or diffusion of adsorbates. The first example of core/shell type PCP single crystals was synthesized by epitaxial growth, and moreover the structural relationship between the shell and the core was determined using surface X-ray diffraction analysis.

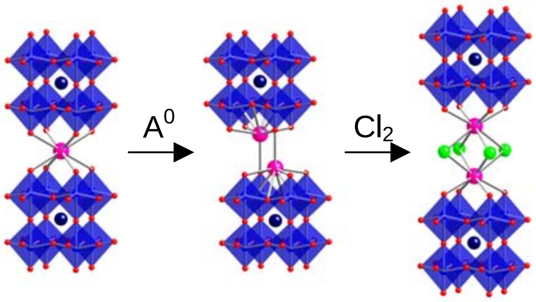
The other approach is to hybridize PCP crystals with other functional organic molecules. The ligand exchange reaction of functional organic molecules with organic linkers that terminate the surfaces of PCP crystals allows us to form the self-assembled monolayers (SAMs) on PCP crystals. Moreover, the in-situ ligand exchange reaction led to the fabrication of nanosized rod-like PCP crystal. The detail mechanism of crystal growth in nanometer scale was unveiled by the time-course measurement of transmission electron microscopy (TEM).

Low Temperature Topochemical Methods for the Construction of Metal-Anion Layers within Perovskite Hosts

Elisha A. Josepha, Jong Lak Choi, Xiao Zhang, Liliana Viciu, Thomas A. Kodenkandath,
and John B. Wiley*
Department of Chemistry and the Advanced Materials Research Institute
University of New Orleans, New Orleans, LA 70148

Low temperature (< 500 °C) topochemical reactions can be an effective way of manipulating the structure and valence of receptive host compounds. Our group is working to develop multistep strategies based on ion exchange and/or intercalation methods for the construction of metal-anion layers within receptive hosts. Previously we have shown that transition-metal-halide layers can be inserted by ion exchange into Dion-Jacobson-type layered perovskites resulting in new oxyhalides such as $(MCl)LaNb_2O_7$ (M = V, Cr, Mn, Fe, Co, Cu). Building on this chemistry, we examined the reductive intercalation of $(CuCl)LaNb_2O_7$. This reaction resulted in the new compounds $(A_xCl)LaNb_2O_7$ (A = Li, Na) with expulsion of copper metal. Subsequent workup of the lithium product resulted in $(Li_2Cl)LaNb_2O_7$. This compound retains the double-perovskite layers of the host, but now contains tetrahedrally-coordinated lithium cations (LiO_2Cl_2) where two alkali-metal layers are separated by a single halide layer.

In an effort to expand this chemistry to larger alkali metals, an alternate strategy based on sequential intercalation reactions has also been investigated. Here a combination of reductive and oxidative intercalations was performed on Dion-Jacobson-type layered perovskites:



This approach has lead to the formation of similarly layered alkali-halide compounds, $(A_2Cl)LaNb_2O_7$ (A = Rb, Cs). Here too, two alkali-metal layers form in the interlayer, but due to the larger sizes of the cations, cubic coordination is favored (AO_4Cl_4).

More recent studies have examined intercalation chemistry with Ruddlesden-Popper layered perovskites, following the examples of Greaves and coworkers.[1] Here oxidative intercalation can be carried. In addition to preparing the already reported Greaves oxyfluoride compounds, we have made some new oxychlorides. Currently we are looking to carryout reductive intercalation in these systems to probe whether alkali-halide arrays can also be formed in these host materials as well.

1. See for example: Li, R.K.; Greaves, C. *Phys. Rev. B* **2000**, *62*, 3811.

Inorganic-organic Hybrids Based on Layered Compounds: Preparation and Applications

Yoshiyuki Sugahara
Department of Applied Chemistry, School of Advanced Science and Engineering,
Waseda University

Inorganic-organic hybrids attract increasing attention, and the use of inorganic nano-building blocks is one of promising preparation methods for these hybrids. It is well known that some inorganic layered compounds, which consist of stacked nano-sheets, can accommodate organic compounds between nano-sheets, leading to the formation of two-dimensional ordered inorganic-organic hybrids. A large number of layered compounds are known to form intercalation compounds with rather weak interfacial interactions, such as ionic bonds, acid-base interactions, and hydrogen bonds. Typical host inorganic layered compounds are clay minerals (for example montmorillonite and kaolinite), protonated forms of layered transition metal oxides and ion-exchangeable layered perovskites. It is also possible to bind organic groups *via* graft reactions when interlayer surfaces possess reactivities. Ion-exchangeable layered perovskites undergo this type of reactions and layered transition metal oxyhalides (MOX, M is typically Fe and Ti) are also well-known host inorganic layered compounds for grafting reactions. Resultant inorganic-organic hybrids can be utilized in several applications, if guest species are functional. For example, the nano-sheets with grafted polyoxyethylene chains can further accommodate $LiClO_4$ and thus exhibited ionic conductivity. Inorganic-organic hybrids can also be converted into nano-structured inorganic materials. The conversion of n-alkylamine-$H_2W_2O_7{\bullet}xH_2O$ hybrids into WO_3 nano-plates is a recent example.