3rd CCS-CSJ, Young Chemists Forum
–Effective Utilization of Elements and its Chemical Applications–

- Date: March 24th (SUN) 9:00-17:10
- Venue: Room S9(CO-LEARNING HOUSE II C601)
  Ritsumeikan University, Biwako-kusatsu Campus(Shiga, Japan)
- Hosted by The Chemical Society of Japan (CSJ)
- Co-hosted by Chinese Chemical Society (CCS)

■9:00-09:10 Opening Remarks from CSJ

(I) Bio-related System and Asymmetric Synthesis

□Chair: ShouFei Zhu

L-1 9:10-9:35 **Sanzhong Luo** (Institute of Chemistry, CAS) page1
"Asymmetric Doubly Covalent Catalysis with Chiral In(III) –Phosphoric Acid Binary Catalyst"

L-2 9:35-10:00 **Lei Liu** (Tsinghua University) page3
"Studies on Protein Chemical Synthesis"

L-3 10:00-10:25 **Hideki Hashimoto** (Okayama University) page5
"Structural Analysis of Nanometric Amorphous Iron Oxide Produced by Iron-oxidizing Bacterium, Leptothrix ochracea"

L-4 10:25-10:50 **Nanfeng Zheng** (Xiamen University) page7
"Multilevel Structure Control of Metal Nanocrystals for Catalysis and Bioapplications"

■10:50-11:00 Coffee Break

(II) Carbon Material: Synthesis, Application, Simulation

□Chair: Sanzhong Luo

L-5 11:00-11:25 **Hayato Tsuji** (The University of Tokyo) page9
"Novel Carbon Materials toward Efficient Photovoltaics
–Carbon-bridged Phenylenevinylenes and Their Application to Dye-sensitized Solar Cells"

L-6 11:25-11:50 **Wen-Xiong Zhang** (Peking University) page11
"Mechanism-directed Organic and Organometallic Chemistry of Carbodiimides"

L-7 11:50-12:15 **Ryotaro Arita** (The University of Tokyo) page13
"Magneto-orbital Effect without Spin
–Orbit Interactions in a Noncentrosymmetric Zeolite-templated Carbon Structure"

■12:15-13:55 Lunch break

(III) Homogeneous and Heterogeneous Catalysis

□Chair: Hayato Tsuji

L-8 13:55-14:20 **Shou-Fei Zhu** (Nankai University) page15
"Iron-catalyzed Carbene Transfer Reactions"

L-9 14:20-14:45 **Aiwen Lei** (Wuhan University) page17
"Oxidative Coupling: Chemistry between Two "Nucleophiles""

L-10 14:45-15:10 **Qilong Shen** (Shanghai Inst. of Organic Chemistry, CAS) page19
"From Trifluoromethylation to Trifluoromethylthiolation:
Development of New Trifluoromethylthiolated Hypervalent Iodine Reagent"

L-11 15:10-15:35 **Takeshi Fujita** (Tohoku University) page21
"Catalytic Origins of Nanoporous Metal"

■15:35-15:45 Coffee Break

(IV) Coordination and Inorganic Chemistry

□Chair: Takeshi Fujita

L-12 15:45-16:10 **Katsuro Hayashi** (Tokyo Institute of Technology) page23
"Refractory Oxides as Novel Electronics and Ionics Materials"

L-13 16:10-16:35 **Liang Zhao** (Tsinghua University) page25
"Macrocycle-directed Metal Cluster-centered Coordination Self-assembly"

L-14 16:35-17:00 **Yoshiaki Nakamura** (Osaka University) page27
"Si-based Epitaxial Nanodots for Thermoelectric Material"

Welcome Address

Dear Colleagues

Welcome to the 3rd CCS-CSJ Young Chemists Forum, held at the same venue as the 93rd CSJ Annual Meeting, Ritsumeikan University, Biwako-Kusatsu Campus, Shiga Prefecture located by the shore of Lake Biwa, under the co-sponsorship of the Chemical Society of Japan (CSJ) and the Chinese Chemical Society (CCS).

This series of bilateral meetings started as a result of an international cooperation agreement between CCS and CSJ signed on March 28, 2009 during the CSJ 89th Annual Meeting. At that time, the leadership of both societies had mutual concerns that opportunities to communicate between younger chemists in China and Japan are much less than those of senior chemists, and agreed that we should in principle provide them with meaningful opportunities to meet face to face. After considerable discussion, we finally agreed a basic structure. It was decided that the forum should be held periodically, for example during annual meetings, and high-level scientists under the age of 45 should be invited.

The first event was held at Xiamen University in June, 2010, followed by the second in April, 2012 at Sichuan University with the themes “Low Dimension Nano Carbon Materials” and “Electrochemical Energy Conversion and Storage” respectively at the CCS Annual Meetings.

The second was originally planned to be held at the CSJ 91st Annual Meeting late March 2011 at Kanagawa University, which the CSJ was expected to host for the first time, but unfortunately, it had to be cancelled because of the March 11 natural disasters. In accordance with the original plan the forum will be held at this 93rd Annual Meeting with the theme “Effective Utilization of Elements and Chemical Applications”.

I would like to thank the symposium chairs Prof. Sanzhong Luo, the Chinese Academy of Science and Prof. Hayato Tsuji, The University of Tokyo, and CCS Executives Prof. Zhongfan Liu, Beijing University and Prof. Zhigang Shuai, Tsinghua University as well as CSJ Executive Director Mr. Nobuyuki Kawashima, for their great efforts to make this symposium possible.

For this symposium sixteen distinguished chemists, nine from China and seven from Japan, will present their research progress and exchange ideas for further development under the above-mentioned theme. Effective utilization of elements is effectively more of a global than local issue for sustainable development worldwide, and I believe that basic science will play an important role. It is my hope that this bilateral symposium will contribute greatly not only to the rapid development of this field but also to development of applications. I also have great expectations that all of the attendants will strengthen their friendships and find new colleagues throughout the symposium for further collaboration.

Kohei Tamao

玉尾皓平

President
The Chemical Society of Japan

Welcome Address

On behalf of the Chinese Chemical Society, I would like to express my sincere greetings to all of the participants of the 3rd China-Japan Young Chemist Forum.

Chinese Chemical Society has a long history of co-operation and exchange with Chemical Society of Japan. In recent years the relations between our two societies have become closer than ever before with more frequent bilateral exchanges.

As the best example, the China-Japan Young Chemist Forum provides an important platform for young chemists from both sides to exchange ideas and collaborate on the variety of topics. After two meetings successfully held in 2010 and 2012, we are very glad to send a delegation consisting of our outstanding young chemists to visit Japan and meet with outstanding Japanese youth for the first time.

We do believe that through the forum these young chemists will not only spark on research ideas, but also make more precious friends for their chemistry career.

Thank the organizing committee for their excellent work. Wish success of the forum and wish all of the participants happy and healthy.

姚建年

Jiannian Yao, President

The Chinese Chemical Society

Sanzhong Luo

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Educational Background

1999	B. Sc., Dept. of Chemistry, Zhengzhou University
2002	M. Sc., Dept. of Chemistry, Nankai University (supervisor: Prof. Jin-Pei Cheng)
2005	Ph.D, Institute of Chemistry & Ohio State University (supervisor: Prof. Jin-Pei Cheng & Peng G. Wang)

Professional Career

2005	Assistant Professor, ICCAS
2008	Associate Professor, ICCAS
2009	CAS visiting scholar, Stanford University (Prof. B. M. Trost)
2011	Professor, ICCAS

Research Interests

Our primary research goal is to invent and develop novel enantioselective catalysts that enable transformations with fundamental synthetic interests and broad utility. We're particularly interested in the development of viable small molecular catalysts that operate through novel activation modes using bio-inspired principles and strategies.

Awards

2011	Thieme Journal Award
2011	Asia Core Program Lectureship
2010	National Science Fund for Distinguished Young Scholar
2009	Lu Jiaxi Young Scientist Award of the Chinese Academy of Science
2008	Young Chemist Award of the Chinese Chemical Society
2007	Rising Star of Science and Technology Research in Beijing

Recent Publications

1. "Chiral Primary Amine Catalyzed Enantioselective Protonation via an Enamine Intermediate" Fu, N. K.; Zhang, L.; Li, J. Y.; Luo, S. Z.*, Cheng, J.-P. *Angew. Chem. Int. Ed.* **2011**, *50*, 11451.
2. "Asymmetric Binary Acid Catalysis: A Regioselectivity Switch between Enantioselective 1,2- and 1,4-Addition through Different Counteranions of In (III)" Lv, J.; Zhang, L.; Zhou, Y.; Nie, Z.; Luo, S. Z.; Cheng, J.-P. *Angew. Chem. Int. Ed.* **2011**, *50*, 6610.
3. "Asymmetric Supramolecular Primary Amine Catalysis in Aqueous Buffer: Connections of Selective Recognition and Asymmetric Catalysis" Hu, S.; Li, J.; Jiang, H.; Pan, J.; Luo, S. Z.*, Cheng, J.-P.* *J. Am. Chem. Soc.* **2010**, *132*, 7216.
4. "A Simple Primary-Tertiary-Bronsted Acid Catalyst for Asymmetric Direct Aldol Reactions of Linear Aliphatic Ketones" Luo, S. Z.;* Xu, H.; Li, J. Y.; Zhang, L.; Cheng, J.-P.* *J. Am. Chem. Soc.* **2007**, *129*, 3074.

L-1

Asymmetric Doubly Covalent Catalysis with Chiral In(III)–Phosphoric Acid Binary Catalyst

Sanzhong Luo

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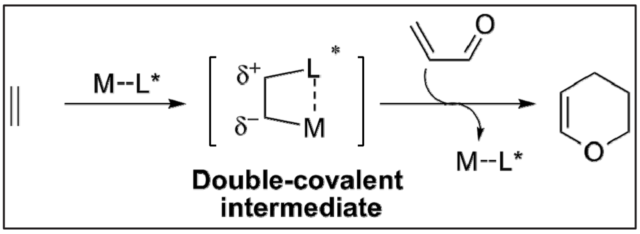
Though catalysis and transformations with simple olefins have been extensively explored, catalytic activation modes with simple olefin are rather limited. We present here a double-covalent activation of simple olefins with both the metal and ligand (phosphoric acid) covalently bonded to a single double bond. This distinctive activation mode enables catalytic enantioselective [4+2] cycloaddition of simple olefins.



Lei Liu

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Educational Background

- 1999 B.Sc., University of Science and Technology of China
- 2004 PhD, Columbia University (supervisor: Prof. R. Breslow)
- 2004-2007 Research Associate, Scripps Research Institute (supervisor: Prof. C.-H. Wong)

Proffesional Career

- 2007 Professor, Tsinghua University

Research Interests

Protein chemical synthesis and its applications.

Awards

- 2002 Arun Guthikonda Memorial Fellow, Columbia University, USA
- 2004 Hammett Award, Columbia University, USA
- 2006 Skaggs Scholar, the Scripps Research Institute, USA
- 2007 First Prize in Natural Science, Ministry of Education, China
- 2008 Li Foundation Heritage Prize, USA
- 2009 Bayer Investigator, Bayer Inc.
- 2010 Thieme Synlett/Synthesis Journal Award

Recent Publications

1. “Protein chemical synthesis by ligation of peptide hydrazides”, Fang, G.-M.; Li, Y.-M.; Shen, F.; Huang, Y.-C.; Li, J.-B.; Lin, Y.; Cui, H.-K.; **Liu, L.**; *Angew. Chem. Int. Ed.* **2011**, *50*, 7645-7649.
2. “Ligation of expressed protein alpha-hydrazides via genetic incorporation of an alpha-hydroxy acid”, Li, Y.-M.; Yang, M.-Y.; Huang, Y.-C.; Li, Y.-T.; Chen, P. R.; **Liu, L.**; *ACS Chem. Biol.* **2012**, *7*, 1015-1022.
3. “Convergent chemical synthesis of proteins by ligation of peptide hydrazides”, Fang, G.-M.; Wang, J.-X.; **Liu, L.**; *Angew. Chem. Int. Ed.* **2012**, *51*, 10347-10350.

L-2

Studies on Protein Chemical Synthesis

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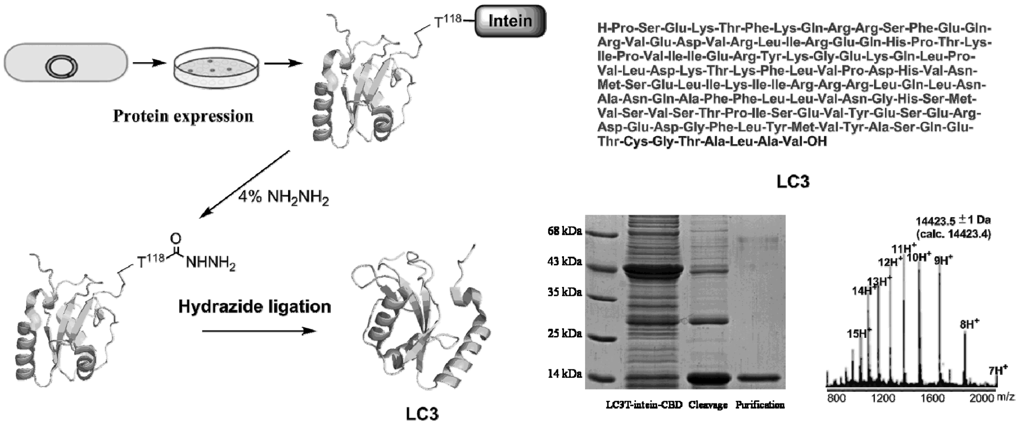
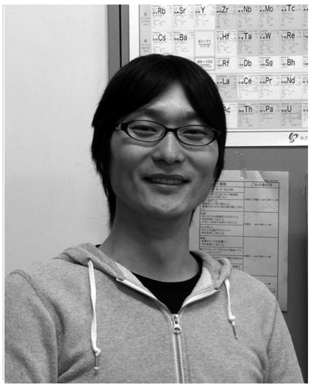
Protein chemical synthesis is a fundamental problem at the interface of chemistry and biology. We found some new reactions in this field including the ligation of protein hydrazides and irreversible N–S acyl transfer reaction. These new methods enable the chemical synthesis of several biomedicinally interesting proteins.



Hideki Hashimoto



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Educational Background

- 2005 Bachelor of Engineering in Department of Applied Chemistry, Faculty of Engineering, Okayama University, Japan
  (supervisor: Prof. Jun Takada)
- 2006 Master of Engineering in Division of Chemical and Biological Technology, Graduate School of Natural Science and Technology, Okayama University, Japan
  (supervisor: Prof. Jun Takada)
- 2009 Ph.D in Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Japan
  (supervisor: Prof. Jun Takada)

Professional Career

- 2008 Research Fellow of the Japan Society for the Promotion of Science (JSPS Research Fellow)
- 2009 Assistant professor, Okayama University

Research Interests

Inorganic/organic hybrid materials produced by microorganisms and their applications for functional materials

Awards

- 2010 The Award for Young Scientist, Okayama Foundation for Science and Technology
- 2012 The Award for Conference 2012, Japan Society of Colour Material

Recent Publications

1. H. Hashimoto, T. Fujii, M. Nakanishi, Y. Kusano, Y. Ikeda, J. Takada, *Mater. Chem. Phys.* **2012**, *136*, 1156–1161.
2. H. Hashimoto, T. Fujii, S. Kohara, H. Asaoka, Y. Kusano, Y. Ikeda, M. Nakanishi, Y. Benino, T. Nanba, J. Takada, *Mater. Chem. Phys.* **2012**, *137*, 571–575.
3. H. Hashimoto, H. Asaoka, T. Nakano, Y. Kusano, H. Ishihara, Y. Ikeda, M. Nakanishi, T. Fujii, T. Yokoyama, N. Horiishi, T. Nanba, J. Takada, *Dyes and Pigments* **2012**, *95*, 639–643.
4. Y. Nishina*, H. Hashimoto*, N. Kimura, N. Miyata, T. Fujii, B. Ohtani, J. Takada, *RSC Advances* **2012**, *2*, 6420–6423. *These authors are equally contributed to this work.
5. T. Suzuki, H. Hashimoto, N. Matsumoto, M. Furutani, H. Kunoh, J. Takada, *Appl. Environ. Microbiol.* **2011**, *77*, 2877–2881.
6. H. Hashimoto, S. Yokoyama, H. Asaoka, Y. Kusano, Y. Ikeda, M. Seno, J. Takada, T. Fujii, M. Nakanishi, R. Murakami, *J. Magn. Magn. Mater.* **2007**, *310*, 2405–2407.

L-3

Structural Analysis of Nanometric Amorphous Iron Oxide Produced by Iron-oxidizing Bacterium, *Leptothrix ochracea*

Hideki Hashimoto,[a] Hiroshi Asaoka,[a] Tomoko Suzuki,[a] Hiromichi Ishihara,[a] Hitoshi Kunoh,[a] Yoshihiro Kusano,[b] Yasunori Ikeda,[c] Masaharu Seno,[a] Makoto Nakanishi,[a] Tatsuo Fujii,[a] Mikio Takano,[d] and Jun Takada[a, e]

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A variety of iron oxides are produced by iron-oxidizing bacteria living in natural aquatic environment. *Leptothrix ochracea* produces an extracellular iron oxide having unique tubular shape of ~1 μm in diameter (Figure 1). In addition to this kind of morphological uniqueness, its compositional and structural features are very intriguing. We have regarded this microbial ceramics as a novel functional material, which we call "*L*-BIOX" (BIOX: biogenous iron oxide). Here we will exhibit the compositional and structural characteristics which are vitally important for future material scientific developments. The present *L*-BIOX microtubules were obtained from an enrichment culture tank using groundwater as the Fe source. The outer surface of the tubular wall is made of fibrillar particles, about 20 nm wide and 50-100 nm long, while the inner surface is made of globular particles of 20–120 nm in diameter. The EDX spectroscopy showed that not only Fe and O but also Si and P are contained considerably, at an atomic ratio of Fe: Si: P = 73: 22: 5. The XRD pattern is similar to that of 2-line ferrihydrite but, unlike ferrihydrite, *L*-BIOX is completely amorphous; the Fourier-transformed HAADF-STEM image showed a halo pattern without any spot, expelling a possibility of nano-scaled structural ordering.

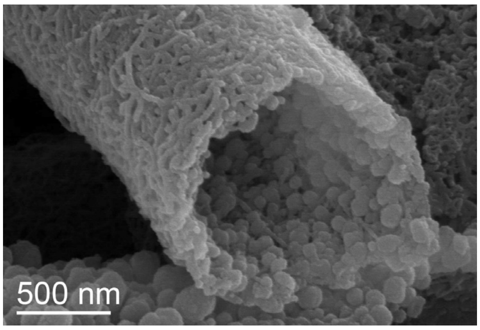

Figure 1. Typical SEM image of iron oxide microtubule produced by an iron-oxidizing bacterium, *Leptothrix ochracea*.

Nanfeng Zheng

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Educational Background

- 1998 B. Sc., Xiamen University, China
- 2005 Ph. D., Inorganic Chemistry, Inorganic Chemistry, University of California –Riverside, (supervisor: Prof. Pingyun Feng)

Professional Career

- 2005. 8-2007. 7 Postdoctoral Research Associate, Department of Chemistry and Biochemistry, University of California – Santa Barbara, with Professor Galen D. Stucky
- 2007. 8- Professor of Xiamen University
- 2010. 3- ChangJiang Chair Professor, Ministry of Education, China

Research Interests

The research interests of Zheng's group focus on functional nanostructures for catalysis and bio-applications, and nanoclusters with well-defined structures. The ultimate goal is to gain deeper understanding of the synthesis, chemical reactivity and also applications of nanostructures at the molecular level. Most of current research efforts of the group are directed to 1) controlled synthesis of noble metal nanocrystals with well-defined exposed surface; 2) tuning metal-inorganic and metal-organic interfaces for catalysis; 3) fabricating hollow mesoporous nanoreactors to enhance the stability of nanoparticulate catalysts; 4) photothermal cancer therapy using nanomaterials.

Recent Publications

1. "Small-adsorbate Assisted Shape Control of Pd and Pt Nanocrystals" Mei Chen, Binghui Wu, Jing Yang, Nanfeng Zheng, *Adv. Mater.* **2012**, *24,* 862–879.
2. " Selective Hydrogenation of *α,β*-Unsaturated Aldehydes Catalyzed by Amine-capped Platinum–Cobalt Nanocrystals" Binghui Wu, Huaqi Huang, Jing Yang, Nanfeng Zheng, Gang Fu, *Angew. Chem. Int. Ed.* **2012**, *51*, 3440-3443.
3. "Carbon Monoxide-assisted Synthesis of Single-crystalline Pd Tetrapod Nanocrystals through Hydride Formation" Yan Dai, Yueming Tan, Nanfeng Zheng, Gang Fu , *J. Am. Chem. Soc.* **2012**, *134*, 7073–7080.
4. "Hollow Mesoporous Aluminosilica Spheres with Perpendicular Pore Channels as Catalytic Nanoreactors" Xiaoliang Fang, Zhaohui Liu, Ming-Feng Hsieh, Mei Chen, Pengxin Liu, Cheng Chen, Nanfeng Zheng, *ACS Nano* **2012**, *6*, 4434–4444.
5. "Graphene–Platinum Nanoparticles-ionic Liquid Composite Catalyst for Methanol-tolerant Oxygen Reduction Reaction" Yueming Tan, Chaofa Xu, Guangxu Chen, Nanfeng Zheng, Qingji Xie, *Energy Environ. Sci.* **2012**, 5, 6923–6927.
6. "Freestanding Palladium Nanosheets with Plasmonic and Catalytic Properties" Xiaoqing Huang, Shaoheng Tang, Xiaoliang Mu, Yan Dai, Guangxu Chen, Zhiyou Zhou, Fangxiong Ruan, Zhilin Yang, Nanfeng Zheng*, *Nat. Nanotech.* **2011,** 6, 28-32.
7. "Etching Growth under Surface Confinement: An Effective Strategy to Prepare Mesocrystalline Pd Nanocorolla" Xiaoqing Huang, Shaoheng Tang, Jing Yang, Yueming Tan, Nanfeng Zheng, *J. Am. Chem. Soc.* **2011,** *133,* 15946–15949
8. "Enhancing the Photothermal Stability of Plasmonic Metal Nanoplates by a Core-Shell Architecture" Xiaoqing Huang, Shaoheng Tang, Biju Liu, Bin Ren, Nanfeng Zheng *Adv. Mater.* **2011**, *23,* 3420-3425.
9. "Amine-Assisted Synthesis of Concave Polyhedral Platinum Nanocrystals Having {411} High-Index Facets" Xiaoqing Huang, Zipeng Zhao, Jingmin Fan, Yueming Tan, Nanfeng Zheng, *J. Am. Chem. Soc.* **2011,** *133,* 4718–4721.

L-4

Multilevel Structure Control of Metal Nanocrystals for Catalysis and Bioapplications

Nanfeng Zheng

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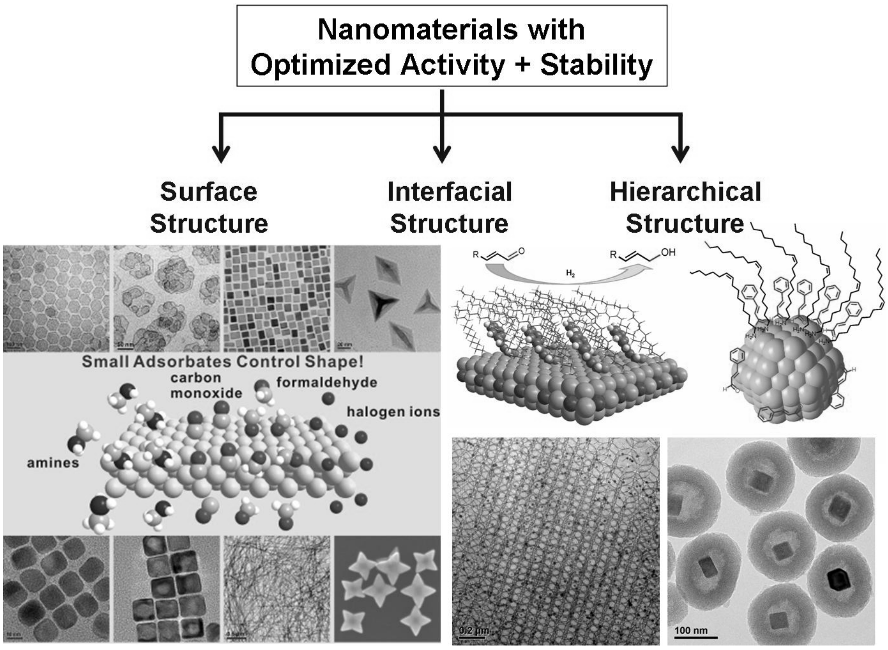
Much of our research effort has been directed towards the development of effective methods to control the surface, interfacial and also hierarchical structures of inorganic nanomaterials. In this presentation, I will provide an overview of our recent research in the following three areas: 1) the controlled synthesis of Pt/Pd nanocrystals with well-defined surface structures using small adsorbates (e.g., CO, halides, organic amines) that preferentially adsorb on specific Pt/Pd surface; 2) the effects of surface structure and interfacial structure of noble metal nanocrystals on their catalysis and bioapplications; 3) the design and fabrication of hollow mesoporous structures. I will first discuss how small adsorbates can be used to control the surface structure of Pd/Pt nanocrystals. For example, halides strongly adsorb on Pd {100} and thus promote the selective production of Pd nanocubes and Pd nanowires with {100} exposed facets. CO molecules behave differently in the controlled synthesis of Pd and Pt nanostructures. CO prefers to adsorb on Pd {111} surface to facilitate the growth of ultrathin Pd nanosheets and tetrapod/tetrahedral nanocrystals having {111} as the main exposure surface. But for Pt, the preferential adsorption of CO on Pt {100} induces the formation of Pt nanocubes. The strong adsorption of amines on Pt stepped sites help the formation of high-index {411} faceted Pt nanocrystals displaying an excellent electrocatalytic activity. Besides the surface structure control and their applications of the shape-controlled metal nanocrystals, the control over the interfacial and hierarchical structure of metal nanocrystals for the optimization of their catalysis and bio-properties will be presented in the talk.



Hayato Tsuji

Associate Professor of Chemistry
Department of Chemistry, School of Science,
The University of Tokyo
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Educational Background

- 1998 B. Sc., Kyoto University
  (supervisor: Prof. Tamio Hayashi)
- 1998 M. Sc., Graduate School of Science, Kyoto University
  (supervisor: Prof. Tamio Hayashi)
- 2001 Doctor of Engineering, Graduate School of Engineering, Kyoto University
  (supervisor: Prof. Kohei Tamao)

Professional Career

- 2001 JSPS Fellowship (PD)
- 2002 Assistant professor, Kyoto University
- 2006 Associate professor, The University of Tokyo
- 2011 JST-PRESTO Researcher

Research Interests

1. Synthesis of π-conjugated molecules using organometallic reagent.
2. Photophysical and electronic functionality.

Awards

- 2009 Banyu Chemistry Award
- 2010 Incentive Award in Synthetic Organic Chemistry
- 2010 The Young Scientists' Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
- 2011 Thieme Chemistry Journal Award

Recent Publications

1. "New Dyes for Dye-sensitized Solar Cells Featuring a Carbon-bridged Phenylenevinylene Linker" Zhu, X.; Tsuji, H.; Yella, A.; Chauvin, A.-S.; Grätzel, M.; Nakamura, *E. Chem. Commun.* **2013**, *49*, 582.
2. "Naphtho[2,1-*b*:6,5-*b*']difuran: a Versatile Motif Available for Solution-processed Single-crystal Organic Field-effect Transistors with High Hole Mobility" Mitsui, C.; Soeda, J.; Miwa, K.; Tsuji, H.; Takeya, J.; Nakamura, E. *J. Am. Chem. Soc.* **2012**, *134*, 5448.
3. "Synthesis of Tetrasubstituted Alkenes by Stereo- and Regioselective Stannyllithiation of Diarylacetylenes" Tsuji, H.; Ueda, Y.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2010**, *132*, 11854.
4. "Modular Synthesis of 1*H*-Indenes, Dihydro-*s*-Indacene, and Diindenoindacene– A Carbon-bridged *p*-Phenylenevinylene Congener" Zhu, X.; Mitsui, C.; Tsuji, H.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 13596.
5. "Bis(carbazolyl)benzodifuran: A High-mobility Ambipolar Material for Homojunction Organic Light-emitting Diode Devices" H. Tsuji, C. Mitsui, Y. Sato, E. Nakamura, *Adv. Mater.* **2009**, *21*, 3776.
6. "Synthesis and Properties of 2,3,6,7-Tetraarylbenzo[1,2-*b*:4,5-*b*']difurans as Hole-Transporting Material" Tsuji, H.; Mitsui, C.; Ilies, L.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2007**, *129*, 11902.

L-5

Novel Carbon Materials toward Efficient Photovoltaics – Carbon-bridged Phenylenevinylenes and Their Application to Dye-sensitized Solar Cells

Hayato Tsuji[a,b]

[a]*Department of Chemistry, School of Science, The University of Tokyo, Hongo,*
Bunkyo-ku, Tokyo 113-0033, Japan
[b]*JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*
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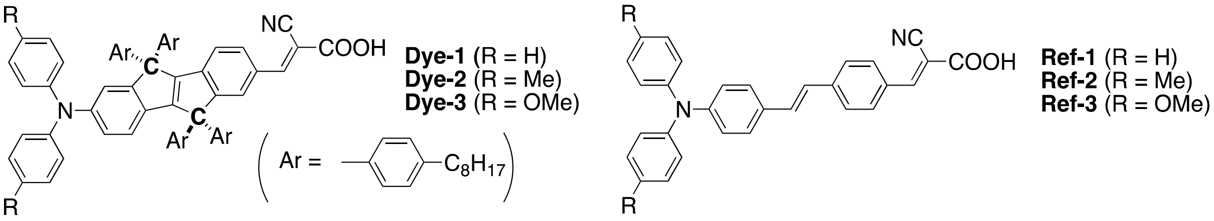
Dye-sensitized solar cells (DSSCs) have achieved a power conversion efficiency (PCE) of ~12% using ruthenium-based dye and are one of the most promising practical photovoltaic devices. From the viewpoint of cost, availability, and toxicity problems of rare metal-based dyes, however, use of metal-free organic dyes has become to attract attention as alternatives. We have been interested in developing new planar π-conjugated systems, and recently found that carbon-bridged phenylenevinylene (COPV) compounds are unique in several aspects among commonly used π-electron systems. In this symposium, I present synthesis and properties of donor-COPV1-acceptor type molecules (**Dye-1** to **Dye-3**, Figure 1) as well as their application to DSSCs to demonstrate their valuable roles to achieve high PCE values for metal-free organic dyes.



Dye-1 (R = H)
Dye-2 (R = Me)
Dye-3 (R = OMe)

Ref-1 (R = H)
Ref-2 (R = Me)
Ref-3 (R = OMe)

Figure 1. COPV1-based dyes (**Dye-1** to **Dye-3**) and reference compounds (**Ref-1** to **Ref-3**) examined in this study.

The PCE values increased progressively from 5.51% (**Dye-1**), to 6.18% (**Dye-2**) and to 7.12% (**Dye-3**), which are 22%, 36% and 43% higher than those obtained for the reference cells using the unbridged conterparts. **Dye-3** gave the highest J_{sc} value of 11.60 mA/cm^2, whereas **Dye-1** and **Dye-2** afforded 9.84 mA/cm^2 and 10.78 mA/cm^2, respectively. This order is in good agreement with that of the absorption maxima. The V_{oc} values for **Dye-1**, **-2** and **-3** systematically increased from 0.745 V (**Dye-1**), to 0.778 (**Dye-2**) and to 0.791 (**Dye-3**), while this is not the case for the reference dyes. As a result, the V_{oc} value for **Dye-3** is higher than that for **Ref-1** by 0.11 V. The V_{oc} value of 0.791 V is remarkably high, given the fact that it is limited by the difference between the oxidation potential of iodide/triiodide and the Fermi level of TiO_2, which is approximately 0.9 V. In addition, the fill factor (FF) of the cells using **Dye-1** to **Dye-3** changes from 0.742, to 0.741 and to 0.763, respectively, values that are much higher than those of 0.68 to 0.70 for the reference cells. An even higher V_{oc} of close to 0.9 V was achieved using a Co(II/III)-based electrolyte, without substantial decrease in other parameters, resulting in the PCE value of 7.54%.

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Educational Background

1992-1996	B. Sc., Hunan Normal University,
1996-2000	M. Sc., Guangxi Normal University (supervisor: Prof. Wenbang Huang)
1999-2002	Ph.D, Nankai University (supervisor: Prof. Li-Cheng Song)
2002–2004	Postdoctoral Fellow, Peking University (supervisor: Prof. Zhenfeng Xi)
2004–2007	Postdoctoral Fellow, Riken, Japan (supervisor: Prof. Zhaomin Hou)

Professional Career

2007-	Professor, Peking University

Research Interests

Structural characterization of active reaction intermediates in metal-mediated or -catalyzed organic synthesis and small molecule activation of novel organo rare earth metal compounds.

Recent Publications

1. "Regioselective Ring Expansion of 2,4-Diiminoazetidines via Cleavage of C–N and C(sp^3)–H bonds: Efficient Construction of 2,3-Dihydropyrimidinesulfonamides" Wang, Y.; Chi, Y.; Zhang, W. -X.;* Xi, Z.* *J. Am. Chem. Soc.* **2012**, *134*, 2926–2929.
2. "Procedure-controlled Selective Synthesis of 5-Acyl-2-iminothiazolines and their Selenium and Tellurium Derivatives by Convergent Tandem Annulation" Wang, Y.; Zhang, W. -X.;* Wang, Z.; Xi, Z.* *Angew. Chem. Int. Ed.* **2011**, *50*, 8122–8126.
3. "Zirconocene and Si-tethered Diynes: A Happy Match Directed towards Organometallic Chemistry and Organic Synthesis" Zhang, W. -X.; Zhang, S.; Xi, Z.* *Acc. Chem. Res.* **2011**, *44*, 541–551.
4. "$Ln_4(CH_2)_4$-Cubane-type Rare-earth Methylidene Complexes Consisting of "$(C_5Me_4SiMe_3)LnCH_2$" Units (Ln = Tm, Lu)" Zhang, W. -X.; Wang, Z.; Nishiura, M.; Xi, Z.;* Hou, Z. *J. Am. Chem. Soc.* **2011**, *133*, 5712–5715.
5. "Efficient One-pot Synthesis of 2,3-Dihydropyrimidinthiones via Multicomponent Coupling of Terminal Alkynes, Elemental Sulfur and Carbodiimides" Wang, Z.; Wang, Y.; Zhang, W. -X.;* Hou, Z.; Xi, Z.* *J. Am. Chem. Soc.* **2009**, *131*, 15108–15109.

L-6

Mechanism-directed Organic and Organometallic Chemistry of Carbodiimides

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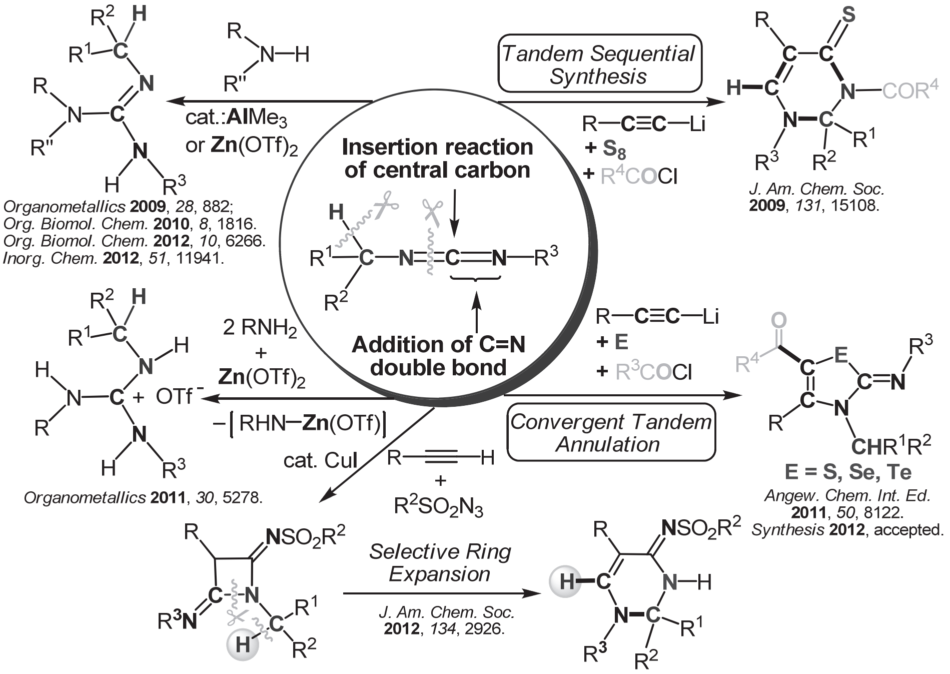
For more than 130 years, carbodiimides (RN=C=NR) have proved versatile reagents since the carbodiimides was first correctly formulated and characterized by Weith. Carbodiimide chemistry mainly included the use as condensing agents in the preparation of nucleotides and peptides, heterocycle synthesis, cycloaddition reactions, biological modification, and etc. For organometallic chemists, carbodiimides were used widely to synthesize amidinate/guanidinate ancillary ligands for stabilization of various metal complexes owing to the well established nucleophilic addition process of organometallic reagents to carbodiimides. Scheme 1 summarized our recent development on the metal-promoted carbodiimide chemistry.[1-4] To gain information on these processes, mechanistic studies were carried out by the isolation and characterization of the important reaction intermediates.



Scheme 1.

References

[1] (a) Xu, L.; Wang, Z.; Zhang, W. -X.;* Xi, Z.* *Inorg. Chem.* **2012**, *51*, 11941. (b) Zhao, F.; Wang, Y.; Zhang, W. -X.;* Xi, Z.* *Org. Biomol. Chem.* **2012**, *10*, 6266. (c) Li, D.; Guang, J.; Zhang, W. -X.;* Wang, Y.; Xi, Z.* *Org. Biomol. Chem.* **2010**, *8*, 1816. (d) Zhang, W. -X.;* Li, D.; Wang, Z.; Xi, Z.* *Organometallics* **2009**, *28*, 882. (e) Li, D.; Wang, Y.; Zhang, W. -X.;* Zhang S.; Guang, J.; Xi, Z.* *Organometallics* **2011**, *30*, 5278.

[2] Wang, Z.; Wang, Y.; Zhang, W. -X.;* Hou, Z.; Xi, Z.* *J. Am. Chem. Soc.* **2009**, *131*, 15108.

[3] Wang, Y.; Zhang, W. -X.;* Wang, Z.; Xi, Z.* *Angew. Chem. Int. Ed.* **2011**, *50*, 8122.

[4] Wang, Y.; Chi, Y.; Zhang, W. -X.;* Xi, Z.* *J. Am. Chem. Soc.* **2012**, *134*, 2926.

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➢ Educational Background

- 1995 B. Sc., The University of Tokyo (supervisor: Prof. Hideo Aoki)
- 1997 M. Sc., Graduate School of Science, The University of Tokyo (supervisor: Prof. Hideo Aoki)
- 2000 Doctor of Science, Graduate School of Science, The University of Tokyo (supervisor: Prof. Hideo Aoki)

➢ Professional Career

- 1999 JSPS Fellowship (DC2)
- 2000 Assistant Professor, The University of Tokyo
- 2006 Research Scientist, RIKEN
- 2008 Assoicate Professor, The University of Tokyo
- 2011 JST-PRESTO Researcher

➢ Research Interests

1. Theoretical materials design of strongly correlated electron systems.
2. Development of new methods for electronic structure calculation.

➢ Awards

- 2006 JDZB Science Award, The Society of Friends of the Japanese-German Center Berlin
- 2011 Young Scientist Award of the Physical Society of Japan
- 2012 The Young Scientists' Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology

➢ Recent Publications

1. "Magneto-orbital Effect without Spin−Orbit Interactions in a Noncentrosymmetric Zeolite-templated Carbon Structure" Koretsune, T.;Arita, R.; Aoki, H. *Phys. Rev. B* **2012**, *86*, 125207.
2. "*Ab initio* Derivation of Electronic Low-energy Models for C_{60} and Aromatic Compounds" Nomura, Y.; Nakamura, K.; Arita, R *Phys. Rev. B* **2012**, *85*, 155452.
3. "*Ab initio* Derivation of Correlated Superatom Model for Potassium Loaded Zeolite" Nohara, Y.; Nakamura, K.; Arita, R *J. Phys. Soc. Jpn.* **2011**, *80*, 124705.
4. "Spin-density-functional Study of the Organic Polymer Dimethylaminopyrrole: A Realization of the Organic Periodic Anderson Model" Suwa, Y.; Arita, R.; Kuroki, K; Aoki, H. *Phys. Rev. B* **2010**, *82*, 235127.
5. "Spin-density-functional Study of Magnetism in Potassium-loaded Zeolite A" Nohara, Y.; Nakamura, K.; Arita, R. *Phys. Rev. B* **2009**, *80*, 220410(R).
6. "First-principles Electronic Structures of Solid Picene" Kosugi, T.; Miyake, T.; Ishibashi, S.; Arita, R; Aoki, H. *J. Phys. Soc. Jpn.* **2009**, *78*, 113704.
7. "*Ab initio* Derivation of Low-energy Model for Alkali-cluster-loaded Sodalites" Nakamura, K.; Koretsune, T.; Arita, R. *Phys. Rev. B* **2009**, *80*, 174420.

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Magneto-orbital Effect without Spin–Orbit Interactions in a Noncentrosymmetric Zeolite-templated Carbon Structure

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A peculiar manifestation of orbital angular momentum is proposed for a zeolite-templated carbon system, $C_{36}H_9$. The structure, being a network of nanoflakes in the shape of a “pinwheel,” lacks inversion symmetry. While the unit cell is large, the electronic structure obtained with a first-principles density-functional theory and captured as an effective tight-binding model in terms of maximally localized Wannier functions, exhibits an unusual feature that the valence band top comes from two chiral states having orbital magnetic momenta of ±1. The noncentrosymmetric lattice structure then makes the band dispersion asymmetric, as reminiscent of, but totally different from, spin-orbit systems. The unusual feature is predicted to imply a current-induced orbital magnetism when holes are doped.

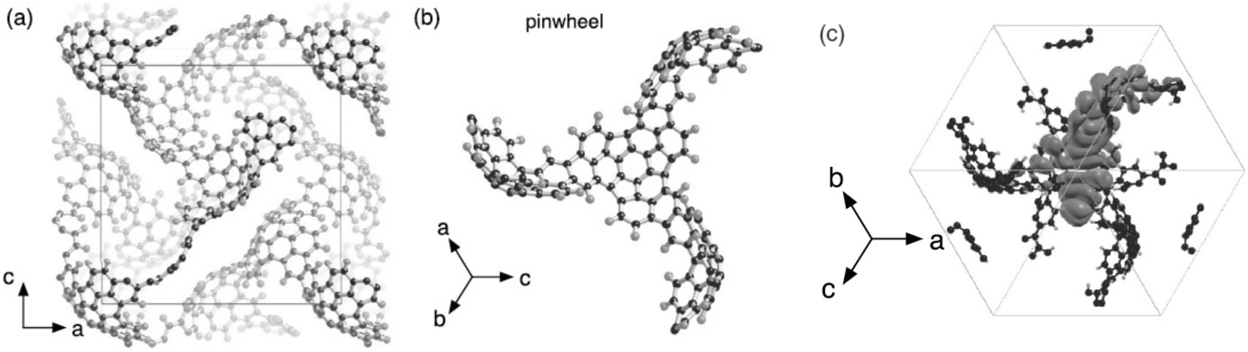

Figure 1. (a) Crystal structure of the zeolite-templated carbon. Solid line represents a unit cell, which contains eight hydrocarbon $C_{36}H_9$ patches [with 288 carbon (darker spheres) and 72 hydrogen atoms (lighter)] with different orientations. (b) A $C_{36}H_9$ patch with its three nearest neighbor patches, which form a three-winged “pinwheel” with a threefold axis. (c) Maximally localized Wannier function for the top valence bands.

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Educational Background

- 2000 B. Sc., Nankai University
  (Advisor: Prof. Shou-He Xiang)
- 2005 Ph. D., Nankai University
  (Advisor: Prof. Qi-Lin Zhou)

Professional Career

- 2005. 7-2008. 12 Lecture, Nankai University
- 2008. 12-present Associate Professor, Nankai University
- 2012. 3-2013. 3 Postdoctoral Fellow, the University of Tokyo
  (Advisor: Prof. Eiichi Nakamura)

Research Interests

SFZ's research interests focus on transition-metal catalysis, particularly on the development of chiral ligands and catalysts as well as new asymmetric reactions. His current research interests involve:
1) Transition-metal-catalyzed asymmetric carbene transfer reactions.
2) Transition-metal/organo cooperative catalysis. 3) Iron catalysis.

Awards

- 2004 Hong Kong Qiu-Shi Award for Graduate Students
- 2007 Tianjin Natural Science Award (the First-Rank)
- 2010 New Century Excellent Talents Project (Ministry of Education of China)
- 2012 The Science Funds for Excellent Youth
  (National Natural Science Foundation of China)
- 2012 The Top-notch Personnel Supporting Project for Youth of China
- 2012 Young Chemist Award of Chinese Chemical Society

Recent Publications

1. "Enantioselective Transition-metal-catalyzed Heteroatom-hydrogen Bonds Insertion Reactions" Shou-Fei Zhu, Qi-Lin Zhou, *Acc. Chem. Res.* **2012**, *45*, 1365–1377**.**
2. "Well-defined Binuclear Chiral Spiro Copper Catalysts for Enantioselective N–H insertion" Shou-Fei Zhu, Bin Xu, Guo-Peng Wang, Qi-Lin Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 436–442.
3. "Enantioselective Hydrogenation of α-substituted Acrylic Acids Catalyzed by Iridium Complexes with Chiral Spiro Aminophosphine Ligands" Shou-Fei Zhu, Yan-Bo Yu, Shen Li, Li-Xin Wang, Qi-Lin Zhou, *Angew. Chem. Int. Ed.* **2012**, *51*, 8872–8875.
4. "Asymmetric N–H Insertion Reaction Cooperatively Catalyzed by Rhodium and Chiral Spiro Phosphoric Acids" Bin Xu, Shou-Fei Zhu, Xiu-Lan Xie, Jun-Jie Shen, Qi-Lin Zhou, *Angew. Chem. Int. Ed.* **2011**, *50*, 11483–11486.
5. "Enantioselective Iron-catalysed O–H Bond Insertions" Shou-Fei Zhu, Yan Cai, Hong-Xiang Mao, Jian-Hua Xie, Qi-Lin Zhou, *Nat. Chem.* **2010**, *2*, 546–551.
6. "Enantioselective Copper-catalyzed Intramolecular O–H Insertion: An Efficient Approach to Chiral 2-Carboxy Cyclic Ethers" Shou-Fei Zhu, Xiao-Guang Song, Yu Li, Yan Cai, Qi-Lin Zhou, *J. Am. Chem. Soc.* **2010**, *132*, 16374–16376.

L-8

Iron-catalyzed Carbene Transfer Reactions

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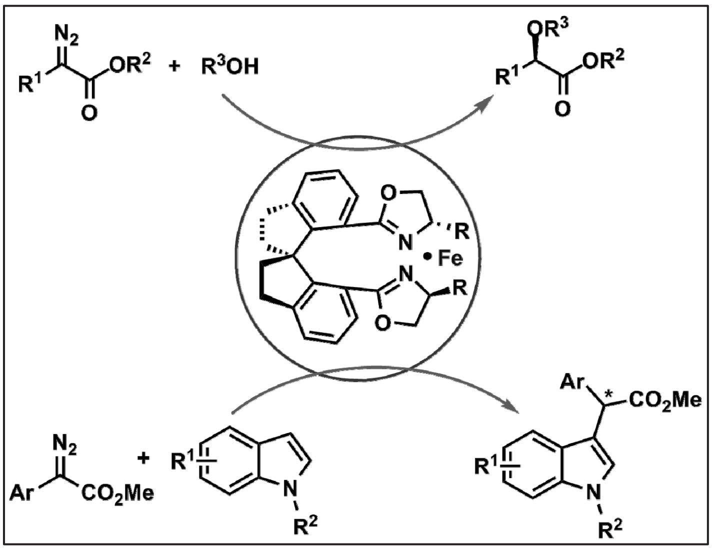
Transition metal catalysis plays a crucial role in modern chemistry. However, the important reactions are predominantly catalyzed by precious metals nowadays. The ready availability, low price, and environmentally benign character of iron imply that it is an ideal alternative to precious metals in catalysis. Recent growth in the number of iron-catalyzed reactions reported reflects an increasing demand for sustainable chemistry. Although tremendous efforts have been devoted into this field in the past decade, the iron catalysis is still in its infancy comparing to well-established precious metal catalysis. The iron catalysis is suffering many challenges, such as limited reaction types, low efficiency, as well as poor selectivity. The development of new iron catalysts and iron-catalyzed new organic transformations are the original impetus for advancing the iron catalysis.

Carbene transfer reactions have been versatile and powerful tools in organic synthesis; however, iron-catalyzed carbene transfer reactions are much underdeveloped. We report here the preliminary results of iron-catalyzed carbene transfer reactions, including O–H bond insertion reactions of alcohols and water, formal C–H bond insertion of indoles, and others. Good to excellent level of enantioselectivities with broad substrate scopes were obtained by fine tune of the chiral iron catalysts. Iron catalysts are superior to other transition metal catalysts in the above reactions, which demonstrate that the iron catalysts are good candidates for asymmetric carbene transformations.



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Educational Background

- 1999-2000 Graduate Studies, Shanghai Institute of Organic Chemistry, CAS, China (SIOC)
- 2000-2003 Postdoctoral Fellow, Department of Chemistry, The Pennsylvania State University (supervisor: Prof. Xumu Zhang)
- 2003-2005 Research Associate, Department of Chemistry, Stanford University (supervisor: Prof. James, P. Collman)

Research Interests

- Small molecule (such as O_2, N_2O, H_2O_2, NH_3, ClO_2^-, etc.) activation with an emphasis on applying such molecules in efficient synthetic methods
- Developing highly selective and efficient transition-metal-catalyzed C–C, and C–Heteroatom bond formation in syntheses
- Mechanistic and active intermediate studies of chlorite dismutase, cytochrome P450, and peroxidase.

Awards

- 2011 Eli Lilly Asian Scientific Excellence Award
- 2011 Lectureship Awardee of Asian International Symposium for Outstanding Young Scientists
- 2010 National Science Fund for Distinguished Young Scholars, China, 2010
- 2009 CAPA (Chinese-American Chemistry & Chemical Biology Professors Association) Distinguished Faculty Award, 2009
- 2008 Chinese Chemistry Society－John Wiley Young Chemist Award
- 2008 Royal Society Chemistry Journal Grant
- 2008 Synthesis & Synlett Journal Award
- 2007 Wuxi Pharmtech Biological & Organic Creative Award
- 2007- Luojia Scholarship Professor (Wuhan University)
- 2006 Outstanding Young Scientist of Hubei Province

Recent Publications

1. A. Lei. etc. *Nature Comm.* (2012) DOI: 10.1038/ncomms2196
2. A. Lei. etc. *Angew. Chem. Int. Ed.* (2012) DOI: 10.1002/anie.201206518
3. A. Lei. etc. *Angew. Chem. Int. Ed. 51*, 9547 (2012)
4. A. Lei. etc. *Angew. Chem. Int. Ed. 51*, 5662 (2012)
5. A. Lei. etc. *J. Am. Chem. Soc. 134*, 5766 (2012)
6. A. Lei. etc. *Angew. Chem. Int. Ed. 51*, 5204 (2012)
7. A. Lei. etc. *Angew. Chem. Int. Ed. 51*, 4666 (2012)
8. A. Lei. etc. *Angew. Chem. Int. Ed. 51*, 3638 (2012)
9. A. Lei. etc. *Chem Sci*, *3*, 1211(2012)

L-9

Oxidative Coupling: Chemistry between Two “Nucleophiles”

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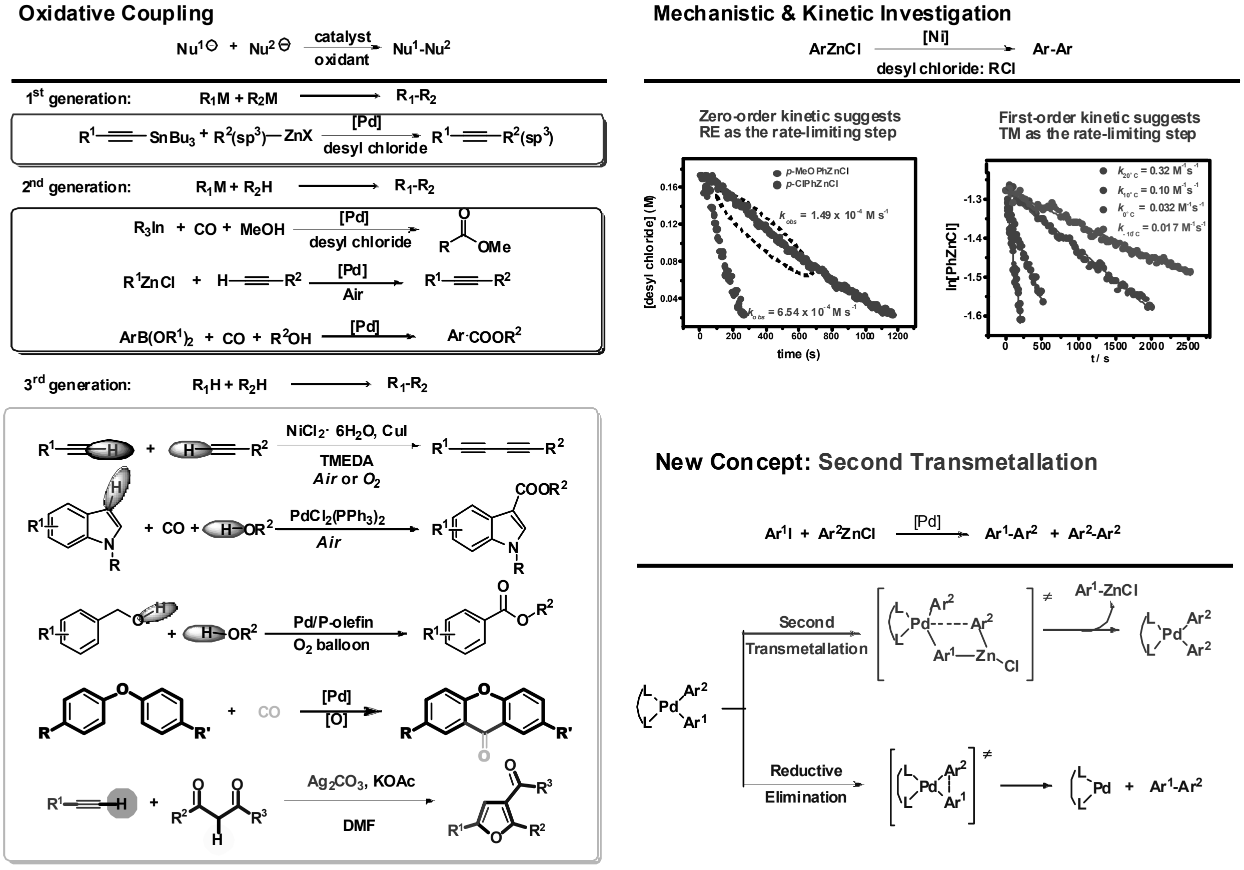
Our research focuses on developing novel and efficient bond-formation methods catalyzed by transition metals. Currently, we are interested in the oxidative coupling, which avoids difficult oxidative addition step and makes bonds between two nucleophiles. As an important character of our research, in-depth understanding toward the reactions is the other focus. Recently, we revealed a second transmetallation reaction, which could occur in the Pd-catalyzed coupling reaction as a fundamental step. In addition, kinetic studies in our laboratory quantitatively disclosed the rate of reductive elimination of Csp^2–Ni–Csp^2.



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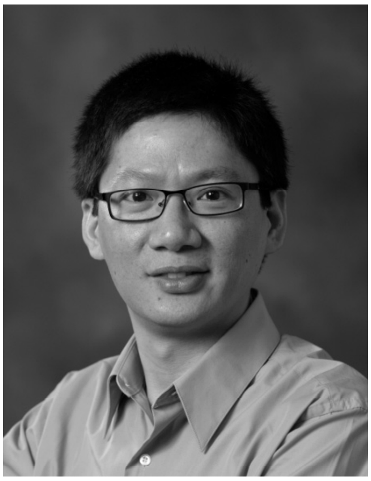

Educational Background

1992-1996	B.S. Nanjing University
1996-1999	M.S. Shanghai Institute of Organic Chemistry, CAS (supervisor: Prof. Long Lu)
2000-2002	M.S. University of Massachusetts, Dartmouth (supervisor: Prof. Gerald B Hammond)
2002-2007	Ph.D. Yale University (supervisor: Prof. John F Hartwig)

Professional Career

2007-2010	Post-doctoral researcher, Department of Chemistry, University of Illinois Urbana-Champaign
2010- present	Professor, Shanghai Institute of Organic Chemsitry, CAS 2001 JSPS Fellowship (PD)

Research Interests

1. Transition metal-catalyzed fluorination and fluoroalkylation of arene, alkene and alkane substrates.
2. Fluoroalkyl-substituted phosphine ligands as CO mimics for asymmetric reactions
3. New methods for the synthesis of fluorinated polymers.

Awards

2013	Thieme Chemistry Journal Award

Recent Publications

1. "An Electrophilic Hypervalent Iodine Reagent for Trifluoromethane-sulfanylation" Shao, X.-X.; Wang, X.-Q.; Yang, T.; Lu, L.; Shen, Q. *Angew. Chem. Int. Ed.* Accepted.
2. "Copper-mediated Aerobic Fluoroalkylation of Arylboronic Acids with Fluoroalkyl Iodides at Room Temperature" Qi Q.; Shen, Q.; Lu, L. *J. Am. Chem. Soc.* **2012**, *134*, 6548.
3. "Highly Selective Trifluoromethylation of 1,3-Disubstituted Arenes through Iridium-catalyzed Arene Borylation" Liu, T.; Shao, X.; Wu, Y.; Shen, Q. *Angew. Chem. Int. Ed.* **2012**, *51*, 540.

L-10

From Trifluoromethylation to Trifluoromethylthiolation: Development of New Trifluoromethylthiolated Hypervalent Iodine Reagent

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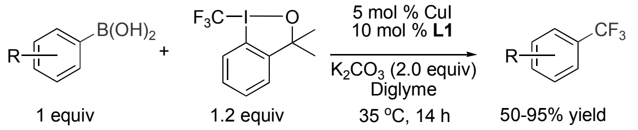
It is well established that the replacement of a hydrogen atom with fluorine in organic compounds brings about major biological and chemical changes. Among many fluorinated functional groups, the trifluoromethyl group (CF_3-) and trifluoromethylthio group (CF_3S-) are two of the most lipophilic substituents. It is well known that incorporation of trifluoromethyl or trifluoromethylthio group into small molecules greatly enhances its ability to cross lipid membranes and in vivo absorption rate. In addition, their high electronegativity significantly improves the small molecule's stability in acidic environments. Thus, both trifluoromethyl and trifluoromethylthio group have been of special attention from pharmaceutical and agrochemical industry for theirs use\ in isosetere-based drug design. Although several strategies employing transition-metal catalysts emerged for the preparation of trifluoromethyl- or trifluoromethylthio-substituted arenes in the past several years, the development of general catalytic methods for the incorporation of these two groups under mild conditions remains a challenge for synthetic organic chemists.

In 2011, we reported a copper-catalyzed protocol for trifluoromethylation of aryl and alkenylboronic acids with trifluoromethylated hypervalent iodine reagent (Togni's reagent). The reaction proceeded in good to excellent yields for a range of different substrates including heteroarylboronic acids and substrates with a variety of functional groups under mild reaction conditions. In addition, we further developed a sequential iridiumcatalyzed C-H activation borylation and copper-catalyzed trifluoromethylation of arenes with a variety of functional groups. The advantage of this tandem procedure was demonstrated by application in a number of biologically active molecules. Based on these results, we envisioned that a trifluoromethylthiolated hypervalent iodine reagent would be a powerful electrophilic reagent for the introduction of trifluoromethylthio group. Herein, we present the invention of such a reagent and its reactions with a variety of nucleophiles such as β-ketoesters, aldehydes, amides, aryl or vinyl boronic acids or alkynes under mild conditions.



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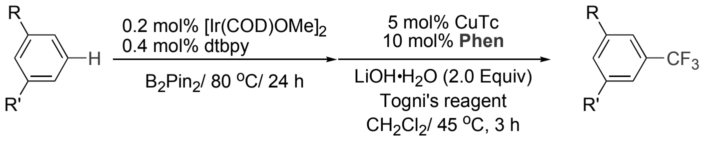

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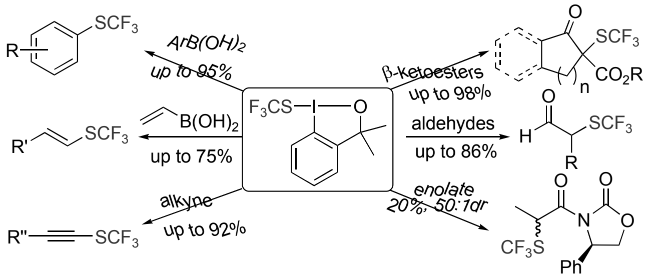
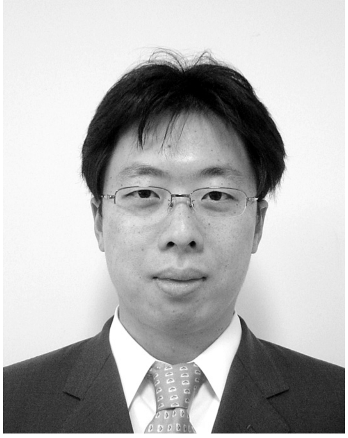


Takeshi Fujita



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➢ Educational Background

- 1998 B. Sc., Kyushu University
  (supervisor: Prof. Minoru Nemoto)
- 2000 M. Sc., Graduate School of Engineering, Kyushu University
  (supervisor: Prof. Minoru Nemoto)
- 2003 Doctor of Engineering, Graduate School of Engineering, Kyushu University
  (supervisor: Prof. Zenji Horita)

➢ Professional Career

- 2003 Assistant Professor, Kyushu University
- 2003 JSPS Postdoctal Fellowship for Research Abroad, Arizona State University
- 2005 Assistant Professor, Tohoku University
- 2010 Associate Professor, Tohoku University
- 2011 JST-PRESTO Researcher

➢ Research Interests

1. Transmission electron microscopy
2. Advanced functional materials (nanoporous metals metallic glass)

➢ Awards

- 2007 JIM Micrograph Award
- 2009 JIM Micrograph Award

➢ Recent Publications

1. "Atomic Origins of the High Catalytic Activity of Nanoporous Gold" T. Fujita, P. F. Guan, K. McKenna, X. Y. Lang, A. Hirata, L. Zhang, T. Tokunaga, S. Arai, Y. Yamamoto, N. Tanaka, Y. Ishikawa, N. Asao, Y. Yamamoto, J. Erlebacher, M. W. Chen, *Nat. Mater.* **2012**, *11*, 775-780.
2. "Nanoporous Metal/Oxide Hybrid Electrodes for Electrochemical Supercapacitors" X. Y. Lang, A. Hirata, T. Fujita, M. W. Chen, *Nat. Nanotechnol.* **2011**, *6*, 232-236.
3. "Oxygen Reduction in Nanoporous Metal–Ionic Liquid Composite Electrocatalysts" J. Snyder, T. Fujita, M. W. Chen, J. Erlebacher, *Nat. Mater.* **2010**, *9,* 904-907.
4. "Atomic-scale Heterogeneity of a Multicomponent Bulk Metallic Glass with Excellent Glass Forming Ability" T. Fujita, K. Konno, W. Zhang, V. Kumar, M. Matsuura, A. Inoue, T. Sakurai, M. W. Chen, *Phys. Rev. Lett.* **2009**, *103*, 075502.
5. "Unusually Small Electrical Resistance of Three-dimensional Nanoporous Gold in External Magnetic Fields" T. Fujita, H. Okada, K. Koyama, K. Watanabe, S. Maekawa, M. W. Chen, *Phys. Rev. Lett.* **2008**, *101,* 166601.
6. "Three-dimensional Morphology of Nanoporous Gold" T. Fujita, L. H. Qian, K. Inoke, J. Erlebacher, M. W. Chen, *Appl. Phys. Lett.* **2008**, *92*, 251902.

L-11

Catalytic Origins of Nanoporous Metal

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It is well known that gold is the only metal that has endothermic oxygen chemisorption energy. In principle, it does not bind oxygen at all and thus is inert toward oxidation reactions. For this reason, the discovery that gold nanoparticles are a catalyst for carbon monoxide (CO) oxidation stimulates extensive research enthusiasms and considerable debate. Because catalytically active gold nanoparticles are usually supported on high surface area oxides, their catalytic performance may be affected by the supports, which has limited the understanding of the intrinsic catalytic activity of gold.

Interestingly, significant catalytic activity can be retained in dealloyed nanoporous gold (NPG) even when their feature lengths are larger than 30 nm. Here we report atomic insights of the NPG catalysis, characterized by Cs-corrected transmission electron microscopy (TEM) and environmental TEM. A high density of atomic steps and kinks are observed on the curved surfaces of NPG, comparable to 3–5 nm nanoparticles, which are stabilized by hyperboloid-like gold ligaments. In situ TEM observations provide compelling evidence that the surface defects are active sites for the catalytic oxidation of CO and residual Ag stabilizes the atomic steps by suppressing {111} faceting kinetics.

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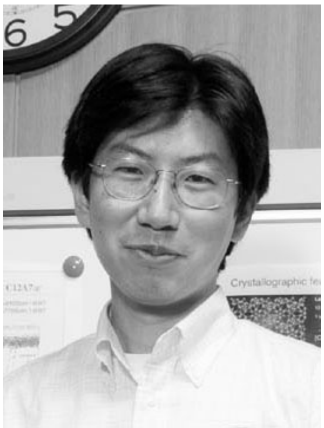

Educational Background

- 1995 B. Sc., The University of Tokyo
- 1997 M. Sc., Graduate School of Engineering, The University of Tokyo
- 2000 Ph. D. (Eng.), Graduate School of Engineering, The University of Tokyo (supervisor: Prof. Taketo Sakuma)

Professional Career

- 1997 JSPS Fellowship (DC1)
- 2000 Postdoctoral Researcher, Hosono Transparent Electro-Active Materials Project, ERATO, JST
- 2004 Assistant Professor, Frontier Collaborative Research Center, Tokyo Institute of Technology
- 2006 Associate Professor, Materials and Structures Laboratory, Tokyo Institute of Technology

Research Interests

1. Electrical and chemical properties of metal-oxide materials
2. Electrochemical devices using solid electrolytes

Awards

- 2006 Young Scientist Award, First International Symposium on Transparent Conducting Oxides (Crete, Greece)
- 2008 Young Scientist Award, MEXT, Japanese Government
- 2009 Third Prize, German Innovation Award Gottfried Wagner Prize 2008
- 2009 Challenging Research Award, Tokyo Institute of Technology

Recent Publications

1. "Intense Atomic Oxygen Emission from Incandescent Zirconia" K. Hayashi, T. Chiba, J. Li, M. Hirano, H. Hosono, *J. Phys. Chem. C*, **2009**, *113* 9436.
2. "Heavy Doping of H^- Ion in $12CaO\cdot7Al_2O_3$" K. Hayashi, *J. Solid State Chem.* **2011**, *184*, 1428
3. "Kinetics of Electron Decay in Hydride Ion-Doped Mayenite" K. Hayashi, *J. Phys. Chem. C*, **2011**, *115*, 11003.
4. "New Functionalities in Ubiquitous Oxides" H. Hosono, K. Hayashi, T. Kamiya, T. Atou, T. Susaki, *Sci. Technol. Adv. Mater.* **2011**, *12*, 34303.
5. "Solid-State Source of Atomic Oxygen for Low-Temperature Oxidation Processes: Application to Pulsed Laser Deposition of TiO_2:N films" D. Ojima, T. Chiba, K. Shima, H. Hiramatsu, H. Hosono, K. Hayashi, *Rev. Sci. Instrum.* **2012**, *83*, 23903.
6. "Thermionic Electron Emission from a Mayenite Electride-Metallic Titanium Composite Cathode" T. Yoshizumi, K. Hayashi, *Appl. Phys. Exp.* **2013**, *6*, 15802.

L-12

Refractory Oxides as Novel Electronics and Ionics Materials

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Typical constitution elements of refractory materials are O, Si, Al, Ca, Mg, Na, Ti, and Zr, which almost agree with the best abundant elements in the Clark's natural abundance. Principal role required for these materials is withstanding severe thermochemical conditions, and many costs cannot be paid for them; they are made of naturally stable and abundant resources i.e. rocks and soils. Although electronic functionality has not been much expected in the refractory materials, a combination of the excellent durability with electronic and/or ionic properties potentially creates novel functionaries and applications without using precious elements. In this symposium, a few research topics of our group according to this policy will be described.

Hydride ion doping in mayenites. Mayenite is a natural mineral as well as a constituent of alumina cements. Its structural formula for the unit cell is described as $[Ca_{24}Al_{28}O_{64}]^{4+}\cdot 4X^-$ ($C_{12}A_7$), in which former part corresponds to a positively charged framework with cage structure and the latter is anions incorporated in the cages (cf. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 872-884).

In 2002, our group reported that the cage anions, $4X^-$, is partially replaced with hydride (H^-) ions by high temperature treatment in hydrogen gas, and resultant H^- ion-doped mayenite is converted to persistently an electronic conductor by irradiation of ultraviolet light. The H^- ion in cage can generate totally two electrons, which again captured in cages, by the photo-assisted reaction via its conversion to H^+ ion, and the electrons are responsible for the conductivity. Since the H^- ion-doped mayenite is transparent, it was expected to serve as a functional transparent oxide conductor (TCO) that potentially substitutes for indium tin oxide (ITO). However, conductivity, transparency, chemical properties and high contact resistance with metals do not meet to requirements for practical applications. Nevertheless the high contact resistance is connected to inherent low work function, which is advantageous for electron emission or injection cathodes. According to thermionic emission property, its work function is as low as 2.1 eV, which is comparable with those of alkali metals.

Although mayenite lattice provide a peculiarly stable site for H^- ion, doping of H^- ion in metal oxide generally has been considered to be very difficult. Since the H^- ion is a strong reducing agent, a host oxide material needs to be durable for it. Refractory materials are good candidates. In addition, there are many oxide-based mineral crystals that have a monovalent anion site like mayenite does. Evidences for H^- ion incorporation in some materials will be also presented.

High energy density battery. Revolutional battery that has an energy density higher by several times than Li-ion batteries is demanded for electronic vehicles having a comparable range with conventional petrol ones. One of the ultimate ways for enhancing the energy density is employment of metallic Li as negative active material and oxygen in air as positive active material. This type of battery is termed Li-air battery and has been studied extensively for the last decade.

We are developing a Na-substituted version for it. The cell is composed of metallic Na negative electrode, organic electrolyte, solid electrolyte, aqueous electrolyte, and gas permeable positive electrode. It is demonstrated that the Na-substitution is not only the replacement with cheaper and more abundant materials but also beneficial for enhancing the energy density. The requirements for the solid electrolyte are fast Na^+ ion conductivity as well as chemical stability for metallic Na and strong basic solutions. We have chosen β-alumina (typical chemical composition of $Na_{1+x}Mg_xAl_{11-x}O_{17}$, where $x \sim 0.6$) and NASICON (typical chemical formula of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, where $x \sim 2.0$) ceramic membranes for this purpose. The cell performance achieved so far will be presented.

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Educational Background

2002	B. Sc., the Chemistry College at Peking University
2003-2007	Ph. D., the Chemistry Department of Chinese University of Hong Kong (supervisor: Prof. Thomas C. W. Mak)
2007-2009	Postdoctoral studies. University of Utah (supervisor: Prof. Peter J. Stang)
2009.11-now	Associate Professor, Department of Chemistry, Tsinghua University
2002.8-2003.7	Research Associate, Institute of Physical Chemistry, Peking University

Research Interests

His research work is focused on (i) synthesis of organic and organometallic macrocycles, (ii) metal cluster-centered coordination self-assembly, (iii) synthesis of high-nuclearity metal clusters and nanoparticles assisted by polydentate organic or organometallic ligands.

Recent Publications

1. “Stabilization of a Reactive Polynuclear Silver Carbide Cluster through the Encapsulation within Supramolecular Cage” Cai-Yan Gao, Liang Zhao*, Mei-Xiang Wang*, *J. Am. Chem. Soc.* **2012**, *134*, 824–827.
2. “Designed Synthesis of Metal Cluster-Centered Pseudo-Rotaxane Supramolecular Architectures” Cai-Yan Gao, Liang Zhao*, Mei-Xiang Wang*, *J. Am. Chem. Soc.* **2011**, *133*, 8448–8451.
3. “Synthesis, Structure and Metal Binding Property of Internally 1,3-Arylene-Bridged Azacalix[6]aromatics” Yi-Xin Fang, Liang Zhao*, De-Xian Wang, Mei-Xiang Wang*, *J. Org. Chem.* **2012**, *77*, 10073–10082.
4. “Designed Synthesis of a Metal Cluster-Pillared Coordination Cage” Xin He, Cai-Yan Gao, Mei-Xiang Wang, Liang Zhao*, *Chem. Commun.* **2012**, *48*, 10877–10879.
5. “Structural Diversity in Coordination Self-Assembled Networks of a Multimodal Ligand Azacalix[4]pyrazine” Jin-Cheng Wu, Liang Zhao*, De-Xian Wang, Mei-Xiang Wang*, *Inorg. Chem.* **2012**, *51*, 3860–3867.
6. “Dual Templated Synthesis of Silver Acetylide Cluster-encapsulated Supramolecular Boxes” Cai-Yan Gao, Xin He, Liang Zhao*, Mei-Xiang Wang*, *Chem. Commun.* **2012**, *48*, 8368–8370.

L-13

Macrocycle-directed Metal Cluster-centered Coordination Self-assembly

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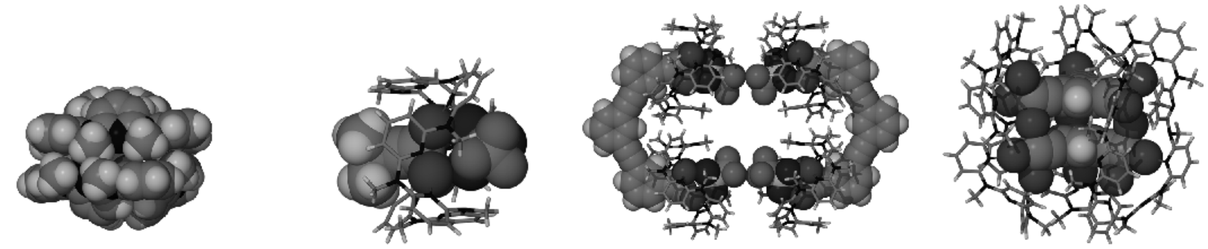
Coordination-driven self-assembly has proven to be a powerful means of synthesizing various discrete supramolecular metallacycles and metallacages.[1] Therein, a single metal atom featuring specific coordination geometry often acts as coordination centers. In contrast, discrete coordination self-assembled metallosupramolecules involving polynuclear metal clusters as centers are scarcely reported to date. In the past two years, we have endeavored to establish a synthetic strategy for the construction of metal cluster-involved supramolecular architectures from zero (0D) to three dimensional (3D). A series of metal cluster-centered supramolecular complexes have been built by silver-acetylide clusters and macrocyclic azacalix[*n*]pyridine ligands.[2-5] Further mechanism studies revealed that the positive homotropic allosteric effect between macrocyclic ligands and metal ions plays a pivotal role in the synthesis of such metal cluster-involved ensembles. This observation facilitated the generalization of this macrocycle-enhanced metal cluster synthetic strategy in the synthesis of metal chalcogenide and halide cluster compounds. Potential applications of these complexes are being extended by us to the following research fields: (i) new metal cluster-based functional materials, (ii) supramolecular catalysts, (iii) supramolecular polymer based on metal cluster-macrocycle building blocks, and (iv) bio-inspired molecular recognition and enzyme mimic.



From single metal-centered to polynuclear metal cluster-centered coordination self-assembly

0D Cluster-Encapsulated Supramolecular Capsule

1D Cluster-Centered Pseudo-Rotaxane

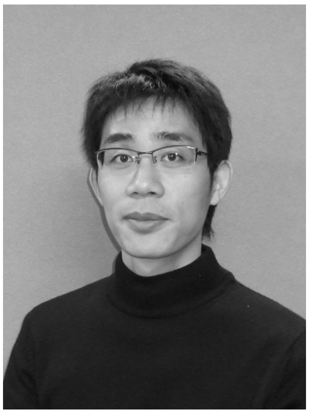
2D Cluster-Centered Metalla-macrocycle

3D Cluster-Centered Metallacage

Reference

1. Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810–6918.
2. Gao, C.-Y.; Zhao, L.*; Wang, M.-X.* *J. Am. Chem. Soc.* **2011**, *133*, 8448–8451.
3. Gao, C.-Y.; Zhao, L.*; Wang, M.-X.* *J. Am. Chem. Soc.* **2012**, *134*, 824–827.
4. Gao, C.-Y.; He, X.; Zhao, L.*; Wang, M.-X.* *Chem. Commun.* **2012**, *48*, 8368–8370.
5. He, X.; Gao, C.-Y.; Wang, M.-X.; Zhao, L.* *Chem. Commun.* **2012**, *48*, 10877–10879.

Yoshiaki Nakamura



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Educational Background

- 1997 B. Eng., Department of Applied. Physics,
  Graduate School of Engineering, The University of Tokyo
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- 1999 M. Eng., Department of Applied. Physics, Graduate School of Engineering,
  The University of Tokyo
  (supervisor: Prof. Koji Maeda)
- 2002 Doctor of Engineering, Department. of Applied. Physics, Graduate School of Engineering,
  The University of Tokyo
  (supervisor: Prof. Koji Maeda)

Professional Career

- 2002 Research Associate: The University of Tokyo
- 2008 Associate Professor: Osaka University
- 2011 JST-PRESTO Researcher

Research Interests

- Optical properties and electronic states of nanodots
- Thermoelectric study on nanodots on Si substrates
- Heteroepitaxy using nanodots
- Resistive switching effect using oxide nanodots

Awards

- 2002 Young Scientist Award in 9th International Workshop on Desorption induced By Electronic Transitions
- 2006 Prize for Lecture Encouragement in The Japanese Society of Applied Physics

Recent Publications

1. "Epitaxial Growth of High Quality Ge Films on Si(001) Substrates by Nanocontact Epitaxy" Nakamura, Y.; Murayama, A.; Ichikawa, M., *Cryst. Growth Des.* **2011**, *11*, 3301.
2. "Nanocontact Heteroepitaxy of Thin GaSb and AlGaSb Films on Si Substrates Using Ultrahigh-density Nanodot Seeds" Nakamura, Y.; Miwa, T.; Ichikawa, M., *Nanotechnology* **2011**, *22*, 265301.
3. "Self-organized Formation and Self-repair of a Two-dimensional Nanoarray of Ge Quantum Dots Epitaxially Grown on Ultrathin SiO_2-covered Si Substrates" Nakamura, Y.; Murayama, A.; Watanabe R.; Iyoda, T.; Ichikawa, M., *Nanotechnology* **2010**, *21*, 095305.
4. "Self-assembled Epitaxial Growth of High Density β-$FeSi_2$ Nanodots on Si (001) and their Spatially Resolved Optical Absorption Properties" Nakamura,Y.; Amari, S.; Naruse, N.; Mera, Y.; Maeda, K.; Ichikawa, M., *Cryst. Growth Des.* **2008**, *8*, 3019.
5. "Quantum-confinement Effect in Individual $Ge_{1-x}Sn_x$ Quantum Dots on Si (111) Substrates Covered with Ultrathin SiO_2 Films Using Scanning Tunneling Spectroscopy" Nakamura, Y.; Masada, A.; Ichikawa, M.; *Appl. Phys. Lett.* **2007**, 91, 013109.
6. "Quantum Fluctuation of Tunneling Current in Individual Ge Quantum Dots Induced by a Single-electron Transfer" Nakamura, Y.; Ichikawa, M.; Watanabe, K.; Hatsugai, Y.; *Appl. Phys. Lett.* **2007**, *90*, 153104.

L-14

Si-based Epitaxial Nanodots for Thermoelectric Material

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Nanostructuring has drawn much attention in thermoelectric study because of reduction effect of thermal conductivity, κ in nanomaterials. In various nanomaterials, we focused on the stacked epitaxial Si nanodot (ND) structures on Si substrates. Our idea is that nanometer-scale interfaces reduce κ drastically and epitaxial growth of crystals can keep electric conductivity σ (Fig. 1). In this paper, we develop the formation technique of the above stacked Si ND structures using ultrathin SiO_2 film technique and measure their thermal conductivity.

Clean Si surfaces were oxidized at 500°C at the O_2 pressure of 2×10^{-4} Pa to form ultrathin (~0.3 nm) SiO_2 films. Si was then deposited to form ultrahigh density ($>10^{12}$ cm^{-2}) Si NDs epitaxially grown on Si substrates as the following. At first stage of Si deposition, nanowindows were created in the ultrathin SiO_2 films through the reaction of $Si + SiO_2 \rightarrow 2SiO\uparrow$, and Si NDs were subsequently formed on the ultrahigh density nanowindows. The above Si ND formation process and oxidization process were repeated to fabricate the stacked Si ND structures.

The epitaxial growth of stacked Si NDs on Si substrates was confirmed by reflection high energy electron diffraction and cross-sectional high resolution transmission electron microscopy. Unlike the nanocomposite, all NDs had almost the same crystal orientation and homogeneously distributed with ultrahigh density. We measured thermal conductivity, κ of these stacked Si ND structures. In the case of 3 nm Si NDs, κ is measured to be ~0.6 W/mK which is below that of Si amorphous (~1-2 W/mK). This demonstrates the possibility of our nanostructure as a Si-based thermoelectric material with high *ZT*.

This work was supported by PRESTO-JST program.

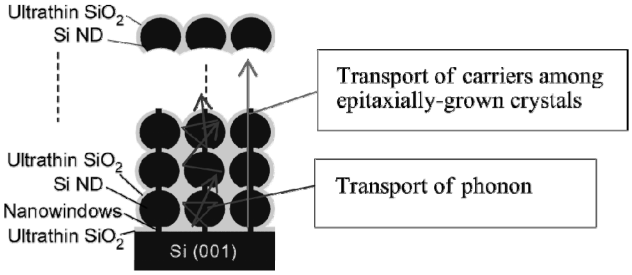

Figure 1. Schematic of stacked epitaxial Si NDs and our idea for κ reduction and σ preservation.

3rd CCS-CSJ, Young Chemists Forum
–Effective Utilization of Elements and its Chemical Applications

- Date: March 24th (SUN) 9:00-17:10
- Venue: Room S9(CO-LEARNING HOUSE II C601)
  Ritsumeikan University, Biwako-kusatsu Campus (Shiga, Japan)

Hosted by
The Chemical Society of Japan
(CSJ) Chinese Chemical
Society (CCS)

Publication： March 2013
Publisher: The Chemical Society of Japan
1-5, Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8307, Japan

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