Graduate School of Advanced Science and Engineering,
Waseda University

博 士 論 文 概 要
Doctor Thesis Synopsis

論 文 題 目

Precisely-Controlled Synthesis of Mesoporous Pt Particles and Films with Various Nanoarchitectures

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May, 2012

Since the discovery of mesoporous materials in the early 1990s, various types have been synthesized under different conditions and thoroughly studied with regard to mesostructural controllability, compositional diversity, and morphological flexibility. The framework compositions that govern the properties of mesoporous materials have been studied most extensively. Mesoporous materials now include a variety of inorganic-based materials, for example, transition-metal oxides, carbon compounds, inorganic-organic hybrid materials, and even metals. Among the many framework compositions, mesoporous metals hold promise for a wide range of potential applications, such as in electronic devices, magnetic recording media, and metal catalysts, owing to their metallic frameworks.

To date, several approaches have been reported for the preparation of mesoporous/mesostructured metals. In a hard-templating method, mesoporous silica with a robust framework and high thermal stability is used as a template to synthesize a metal replica. So far, various Pt nanostructures, such as 1D nanowires and 3D nanowire networks, have been prepared using MCM-41 (*p*6*mm*), SBA-15 (*p*6*mm*), KIT-6 (*Ia*-3*d*), and MCM-48 (*Ia*-3*d*) as hard templates. Despite those recent advances in the hard-templating method, however, the obtained morphologies of mesoporous metals have been limited to only powders with irregular morphology or films on conductive substrates. Lack of controllability of the particle sizes and morphological shapes is a serious problem for further development of mesoporous metals. The shapes and particle sizes critically determine the function and utility for applications. To bring out shape- and size-dependent physicochemical properties, it is extremely important to prepare uniform-sized particles with the same shapes in high yield. On the other hand, lyotropic liquid crystals made of highly concentrated surfactants or block copolymers have been utilized as a soft template. By using chemical or electrochemical reduction, ordered mesoporous metal powder or films can be respectively synthesized. However, the ordered arrangement of the rod-self assemblies in the liquid crystals is often distorted during the metal deposition process, resulting in the lack of a long-range order of mesoporous structures in the final product. In addition, the controllability of the pore sizes in mesoporous metal systems is much more limited than that in mesoporous silica systems. Therefore, the development of a highly reproducible soft-templating method is in much demand.

To overcome the above issues in the soft- and hard-templating methods, I have proposed several novel approaches during my program. In the hard-templating method, I have especially focused on nanoscale metal deposition behaviors inside the mesochannels. By realizing a controlled chemical reduction with appropriate reducing agent, well-defined mesoporous platinum (Pt) nanoparticles were successfully synthesized, which cannot be prepared using other means. In the soft-templating method, I have established new approach using extremely diluted surfactant solutions. Unlike the previous soft-templating methods, it became possible to effectively manipulate various mesopore sizes by simply changing different surfactants and adding organic expanders in the aqueous solution.

Chapter 1 provides background of the thesis, an overview of Pt-based meso/nanoporous materials, and a review of the previous synthetic approaches. The syntheses of the related nanomaterials, such as nanowires, nanotubes, and nanodendrites, are also reviewed. The advantages of a mesoporous structure over other nanostructures are also clarified.

In **Chapters 2**, **3**, and **4**, the use of the hard-templating approach is demonstrated. In **Chapter 2**, as the

first demonstration, mesoporous Co_3O_4 particles are prepared by using mesoporous silica KIT-6 (with double gyroid *Ia*-3*d* symmetry) as a hard template and $Co(NO_3)_2{\cdot}6H_2O$ as an inorganic precursor. Although precious metal catalysts (*e.g.*, Pt, Au) with various morphologies have been generally utilized for the CO oxidation reaction, Co_3O_4 material is well known as an alternative catalyst for low-temperature CO oxidation. In this chapter, the effect of the calcination temperatures (during conversion from Co salts to Co_3O_4 crystals inside mesopores) on the CO oxidation was carefully investigated, as this is an important step in the design process of novel mesoporous Pt catalysts.

In **Chapter 3**, the synthesis of ordered mesoporous Pt nanoparticles with uniform shapes and sizes is demonstrated by employing three-dimensional (3D) bicontinuous mesoporous silica (KIT-6) as a hard template. After a K_2PtCl_4 aqueous solution was introduced into mesoporous silica powders, an ascorbic acid aqueous solution, as a reducing agent, was dropped onto the powder. The obtained mesoporous Pt particles were isolated, and their particle-size distribution was observed to be very narrow. The particle sizes were controllable by changing the reduction times, which is advantageous point over the previous hard-templating method. More interestingly, the Pt replicas showed rhombic dodecahedral morphology. The single crystallinity of the Pt *fcc* structure extended coherently over all of the particles. Low-angle XRD profiles are assignable to *Ia*-3*d*, giving the same profile as for the original KIT-6 mesoporous silica. This is evidence that the replication of Pt from KIT-6 retains the original symmetry.

In **Chapter 4**, this concept is extended to synthesize well-ordered mesoporous Pt nanoparticles with uniform olive shapes by using two-dimensional (2D) hexagonal mesoporous silica (SBA-15) as a hard template. Also, various reducing agents, such as AA, sodium borohydride (SBH), and dimethylaminoborane (DMAB), were applied in this system and different Pt deposition behaviors in the mesoporous matrices were carefully discussed. The Pt deposition rates are determined by the reductive strength of reducing agents. The redox potentials of SBH and DMAB are much lower than that of AA. Therefore, compared with AA, SBH and DMAB are very strong reducing agents and can reduce Pt sources very quickly. Therefore, SBH and DMAB molecules cannot enter inside the mesopores and cannot reduce the Pt species inside the mesoporous silica particles. SBH reduces the Pt species immediately by very severe self-decomposition reaction with a large volume of gas, thereby depositing the Pt outside the mesoporous silica particles. In contrast, the use of AA provides sufficient time to access the Pt sources located inside the mesopore. At the initial stage of the Pt deposition, the AA reduces the Pt species embedded in the mesoporous particles to deposit the Pt nuclei, and the grain growth proceeds continuously from the primary Pt nuclei. Consequently, it was proved that the reaction kinetics was critical for high-quality synthesis. The optimized chemical reduction using AA is vital for the formation of mesoporous Pt nanoparticles with uniform shapes and sizes. Low-angle XRD profiles for the obtained Pt samples showed three distinct peaks assignable to the (10), (11), and (20) planes of a highly ordered 2D hexagonal symmetry. Periodically arranged Pt nanowires were observed; they were a negative replica of the 2D hexagonally ordered mesoporous silica (SBA-15).

In **Chapters 5**, **6**, and **7**, the use of the soft-templating approach for dendritic Pt particles and mesoporous Pt films is demonstrated. These soft-templating approaches use low-concentrated surfactant (or organic molecule) solutions, in contrast to the lyotropic liquid crystalline method which requires very high

surfactant concentrations (over 30 wt %). In **Chapter 5**, a facile synthesis of three-dimensional (3D) branched Pt nanoclusters with high surface area is demonstrated by using simple microwave-assisted heat-treatment of an aqueous solution containing Pt source and hydrophilic molecules. The obtained Pt nanoclusters were self-supporting Pt nanostructures and possessed a very high surface area (41 $m^2 \cdot g^{-1}$). The combination of high surface area with the nanoarchitecture is very advantageous for electrocatalytic applications. However, well-defined mesoporous structures with uniform pore sizes are, unfortunately, not well developed.

To realize the formation of uniformly sized mesopores, in **Chapter 6**, an approach to "electrochemical micelle assembly" is proposed in which a simple electrodeposition method is used in an aqueous surfactant solution. The mesopore sizes in the deposited films could be widely tuned from 5 nm to 30 nm by changing the sizes of the used surfactants and adding a hydrophobic aromatic compound as an expander. With a decrease in the surfactant concentration below CMC, no porous structures were obtained. On the other hand, when the surfactant concentration was over CMC, many spherical mesopores were formed in the films. Based on these data, mesoporous Pt films are expected to be electrodeposited by the assembly of surfactant micelles with metal species. In the plating solution, dissolved Pt ions are coordinated by water molecules to form metal-aqua complexes. Since the coordinated water molecules usually interact with ethylene oxide (EO) groups of the surfactant micelles, the dissolved Pt ions adsorb inside the external EO region of the surfactant micelles. Therefore, during the electrochemical deposition, the Pt species are assumed to move to the working electrode together with the surfactant micelles. Thus, the surfactant micelles act as structural directing agents. Such a facile electrochemical design of mesoporous metals and alloys should greatly contribute to future applications, such as micro-sensors, micro-batteries, micro-bioactive materials, and miniaturized devices.

In **Chapter 7**, this concept is extended to the synthesis of mesoporous alloys such as Pt-Pd. The alloy compositions in the films were successfully synthesized by changing the compositional ratios in the precursor solutions. The framework in the obtained mesoporous films was composed of connected metal nanoparticles (around 3 nm in diameter). Interestingly, the atomic crystallinity was coherently extended across several nanoparticles. Each nanoparticle is in an alloy state and showed a characteristic morphology with an undefined shape with higher index surface, that is, a large number of steps. Thanks to such unique pore walls, the mass-normalized electrochemical performance for methanol electrooxidation was dramatically enhanced (over 100 times) relative to that of non-porous Pt film. Furthermore, this electrochemical process allows easy preparation of other mesoporous Pt-based alloy films with various compositions, which is important for realizing much higher performance as electrodes in batteries.

In **Chapter 8**, general conclusions of this thesis and future prospects are presented. I strongly believe that this study will provide a new generic platform for the preparation of mesoporous metal nanoparticles and films. My synthetic mechanism is expected to generate other metallic and semiconducting mesoporous films with various nanoarchitectures of technological importance for the future. Currently, Pt is widely used as an industrial catalyst and battery electrode due to its usefulness as a durable metal as well as its chemical function as a catalyst in a number of reactions. In view of the strong social demand for reduced use of rare metals, this study will, ideally, become valuable in the effort to secure high functionality with low use of Pt by producing mesoporous structures with larger surface areas.

早稲田大学　博士（工学）　学位申請　研究業績書

(List of research achievements for application of doctorate (Dr. of Engineering), Waseda University)

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（As of 20, April, 2012）

種 類 別(By Type)	題名，発表・発行掲載誌名，発表・発行年月，連名者（申請者含む） (theme, journal name, date & year of publication, name of authors inc. yourself)
(1) Paper	1. Electrochemical Synthesis of Mesoporous Pt-Ru Alloy Films as Superior Electrocatalysts *Chemistry-A European Journal*, accepted. Hongjing Wang and Yusuke Yamauchi 2. All Metal Layer-by-Layer Films: Bimetallic Alternate Layers with Accessible Mesopores for Enhanced Electrocatalysis *Journal of the American Chemical Society*, DOI: 10.1021/ja303773z. (June 20, 2012) Hongjing Wang, Katsuhiko Ariga, and Yusuke Yamauchi ○3. Synthesis of Mesoporous Pt-Pd Alloy Films by Electrochemical Plating in Aqueous Surfactant Solutions *Chemistry-An Asian Journal*, DOI: 10.1002/asia.201200316. (June 25, 2012) Hongjing Wang and Yusuke Yamauchi ○4. Synthesis of Mesoporous Pt Films with Tunable Pore Sizes from Aqueous Surfactant Solutions *Chemistry of Materials*, **2012**, 24, 1591-1598. (April 23, 2012) Hongjing Wang**,** Liang Wang, Takaaki Sato, Yasuhiro, Sakamoto, Satoshi Tominaka, Keiichi Miyasaka, Nobuyoshi Miyamoto, Yoshihiro Nemoto, Osamu Terasaki, and Yusuke Yamauchi 5. Electrochemical Synthesis of Mesoporous Pt-Au Binary Alloys with Tunable Compositions for Enhancement of Electrochemical Performance *Journal of the American Chemical Society*, **2012**, 134, 5100-5109. (February 21, 2012) Yusuke Yamauchi, Akihisa Tonegawa, Masaki Komatsu, Hongjing Wang, Liang Wang, Yoshihiro Nemoto, Norihiro Suzuki and Kazuyuki Kuroda ○6. Synthesis of Olive-Shaped Mesoporous Platinum Nanoparticles (MPNs) with a Hard-Templating Method Using Mesoporous Silica (SBA-15) *Chemistry-An Asian Journal*, **2012**, 7, 802-808. (February 1, 2012) Hongjing Wang**,** Masataka Imura, Yoshihiro Nemoto, Sang-Eon Park, and Yusuke Yamauchi ○7.Shape- and Size-Controlled Synthesis in Hard Templates: Sophisticated Chemical Reduction for Mesoporous Monocrystalline Platinum Nanoparticles *Journal of the American Chemical Society*, **2011**, 133, 14526-14529. (August 30, 2011) Hongjing Wang**,** Hu Young Jeong, Masataka Imura, Liang Wang, Logudurai Radhakrishnan, Nobuhisa Fujita, Toen Castle, Osamu Terasaki, and Yusuke Yamacuhi 8. Direct Synthesis of Nanoporous Carbon Nitride Fibers Using Al-based Porous Coordination Polymers (Al-PCPs) *Chemical Communications*, **2011**, 47, 8124-8126. (June 20, 2011) Ming Hu, Julien Reboul, Shuhei Furukawa, Logudurai Radhakrishnan, Yuanjian Zhang, Pavuluri Srinivasu, Hideo Iwai, Hongjing Wang, Yoshihiro Nemoto, Norihiro Suzuki, Susumu Kitagawa, Yusuke Yamauchi

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(List of research achievements for application of doctorate (Dr. of Engineering), Waseda University)

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	○9. Mesoporous Co_3O_4 for Low Temperature CO Oxidation: Effect of Calcination Temperatures on Their Catalytic Performance *Journal of Nanoscience and Nanotechnology*, **2011**, 11, 3843-3850. (May 1, 2011) Hongjing Wang, Yonghong Teng, Logudurai Radhakrishnan, Nemoto Yoshihiro, Imura Masataka, Shimakawa Yuichi, and Yusuke Yamauchi* ○10. Microwave-assisted Rapid Synthesis of Platinum Nanoclusters with High Surface Area *Journal of Nanoscience and Nanotechnology*, **2010**, 10, 6489-6494. (October 1, 2010) Hongjing Wang, Liang Wang, Yoshihiro Nemoto, Norihiro Suzuki, and Yusuke Yamauchi* 11. A High-Speed Passive-Matrix Electrochromic Display Using a Mesoporous TiO_2 Electrode with Vertical Porosity *Angewandte Chemie-International Edition*, **2010**, 49, 3956-3959. (April 21, 2010) Wu Weng, Tetsuya Higuchi, Masao Suzuki, Toshimi Fukuoka, Takeshi Shimomura, Masotoshi Ono, Logudurai Radhakrishnan, Hongjing Wang, Norihiro Suzuki, Hamid Oveisi, and Yusuke Yamauchi 12. Precise Manipulation of One-Dimensional Mesochannel Alignments in Mesoporous Silica Films by Novel Rubbing Method Utilizing Lyotropic Liquid Crystals *Chemistry-An Asian Journal*, **2010**, 5, 1290-1293. (April 8, 2010) Logudurai Radhakrishnan, Hongjing Wang, and Yusuke Yamauchi 13. Rapid and Efficient Synthesis of Platinum Nanodendrites with High Surface Area by Chemical Reduction with Formic Acid” *Chemistry of Materials*, **2010**, 22, 2835-2841. (March 25, 2010) Liang Wang, Hongjing Wang, Yoshihiro Nemoto, and Yusuke Yamauchi **13 Papers**
(2) Presentation	1. Design of Mesoporous Pt with Superior Electrocatalytic Activity （口頭発表） 第27回ゼオライト研究発表会，大阪，日本（2011年12月1-2日） Hongjing Wang, Hamed Ataee-Esfahani, Masataka Imura, LiangWang, Yoshihiro Nemoto, and Yusuke Yamauchi 2. Shape- and Size-Controlled Synthesis in Hard Templates: Sophisticated Chemical Reduction for Mesoporous Monocrystalline Pt Nanoparticles (Poster presentation) The 3rd NIMS-Waseda International Symposium, Tokyo, Japan (November 1, 2011) Hongjing Wang, and Yusuke Yamauchi 3. Mesoporous Co_3O_4 for Low Temperature CO Oxidation: Effect of Calcination Temperatures on Their Catalytic Performance (Poster presentation) International Symposium on Photocatalysis and Environmental remediation materials, Tsukuba, Japan (January 17-19, 2011) Hongjing Wang, and Yusuke Yamauchi

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	4. Mesoporous Co_3O_4 for Low Temperature CO Oxidation: Effect of Calcination Temperatures on Their Catalytic Performance (Poster presentation) The 2nd NIMS-Waseda International Symposium, Tsukuba, Japan (December 1, 2010) Hongjing Wang, Logudurai Radhakrishnan, and Yusuke Yamauchi 5. Rubbing Method for Mesoporous Silica Films with Uniaxially Oriented Mesochannels Based on Lyotropic Liquid Crystal Approach (Poster presentation) JSPS A3 Foresight Seminar: Present Status and Future Prospects of Mesoporous Materials, Tokyo, Japan (September 3, 2010) Hongjing Wang, Logudurai Radhakrishnan, and Yusuke Yamauchi 6. New Rubbing Method for Mesoporous Silica Films with Uniaxially Oriented Mesochannels Based on Lyotropic Liquid Crystal Approach (Poster presentation) The 4th Global COE International Symposium on 'Practical Chemical Wisdom', Tokyo, Japan. (January 14, 2010) Hongjing Wang, Logudurai Radhakrishnan, and Yusuke Yamauchi **6 Presentations**
(3) Book	1. Chapter 6: Synthesis of Mesoporous Metal Oxides and Metals and Their Applications "Nanoporous Materials: Synthesis and Applications (Taylor & Francis Group)" (To be published in December, 2012) Hongjing Wang, Xiangfen Jiang, and Yusuke Yamauchi