

Graduate School of Advanced Science and Engineering,
Waseda University

博士論文審査報告書

論 文 題 目

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

申 請 者
(Applicant Name)

Hongjing	WANG
王	鴻静

(Major in Nanoscience and Nanoengineering, Research on Synthetic
Chemistry of Nanomaterials)

July, 2012

Since the discovery of mesoporous materials, various types have been synthesized under different conditions and thoroughly studied with regard to mesostructural controllability, compositional diversity, and morphological flexibility. Among the many framework compositions, mesoporous metals hold promise for a wide range of electrochemical applications, such as 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 is used as a template to synthesize a metal replica. Various Pt nanostructures, such as 1D nanowires and 3D nanowire networks, have been prepared using various templates. Despite those recent advances in the hard-templating method, however, the obtained morphologies 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 powders or films can be, respectively, synthesized. However, the ordered arrangement of the hydrophilic domains 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, several novel approaches have been proposed during my program.

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-3d* symmetry) as a hard template. 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. The effect of the calcination temperatures (during conversion of the cobalt salt to Co_3O_4 crystals inside mesopores) on the CO oxidation is carefully investigated. 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 shape and size is demonstrated by employing three-dimensional (3D) bicontinuous mesoporous silica (KIT-6) as a hard template. Especially, nanoscale Pt deposition behaviors inside the mesochannels are focused. By realizing a controlled chemical reduction with appropriate reducing agent (ascorbic acid, AA), well-defined mesoporous platinum (Pt) nanoparticles are successfully synthesized, which cannot be prepared using other means. The obtained mesoporous Pt particles are totally isolated, and their particle-size distribution is observed to be very narrow. The particle sizes are controllable by changing the reduction times, which is advantageous point over the previous hard-templating methods.

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. Various reducing agents, such as AA, sodium borohydride (SBH), and dimethylaminoborane (DMAB), are used in this system and Pt deposition behaviors in the mesoporous matrices are carefully investigated. The Pt deposition rates are determined by the reduction power of the reducing agents. Compared with AA, SBH and DMAB are very strong reducing agents that reduce Pt species very quickly. Therefore, the SBH and DMAB molecules cause reduction mainly outside the pores. 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 and the particles take the shape of the pores around the nuclei. Thus, such a controlled Pt deposition is necessary for high-quality synthesis. Well-defined morphology and uniformity in particle size will become very important aspects for the future use of mesoporous metals in a wide range of applications.

In **Chapters 5, 6, and 7**, the use of the soft-templating approach for dendritic Pt particles and mesoporous Pt films are 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 nanoparticles 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 nanoparticles are self-supporting Pt nanostructures and possessed a very high surface area ($41 \text{ m}^2 \cdot \text{g}^{-1}$). The combination of high surface area with the nano-architecture is very advantageous for electrocatalytic applications. However, well-defined mesoporous structures with uniform pore size are, unfortunately, not yet well demonstrated.

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 has been established by using an aqueous surfactant solution. The pore size in the deposited films can be tuned from 5 nm to 30 nm by changing the sizes of the used surfactants and by adding a hydrophobic aromatic compound as an expander. Through several comparative studies, mesoporous Pt

films are expected to be electrodeposited by the assembly of surfactant micelles with metal species. In the plating solution, the dissolved Pt ions are surrounded by the coordinated water molecules to form metal-aqua complexes. Since the coordinated water molecules usually interact with ethylene oxide (EO) groups of the surfactant micelles, the platinum aqua complex ions are adsorbed inside the external EO region of the surfactant micelles. Therefore, during the electrochemical deposition, the Pt species are thought to move to the working electrode together with the surfactant micelles. Thus, the surfactant micelles act as structural directing agents to self-assemble mesoporous platinum films over the electrode surface. Unlike the previous lyotropic liquid crystalline method, the present plating solutions can be reused several times, demonstrating high repeatability.

In **Chapter 7**, the micelle assembly concept has been extended to the synthesis of mesoporous alloys, such as Pt-Pd. The alloy compositions in the films are successfully synthesized by changing the compositional ratios in the precursor solutions. The framework in the obtained mesoporous films is composed of connected metal nanoparticles (around 3 nm in diameter). Interestingly, the atomic crystallinity is coherently extended across several nanoparticles. Each nanoparticle is in an alloy form and shows 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 is dramatically enhanced (over 100 times) relative to that of non-porous Pt film. This electrochemical process allows easy preparation of other mesoporous Pt-based alloy films with various compositions in future, 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.

This thesis provides a new generic platform for the preparation of mesoporous metal nanoparticles and thin films. 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 less amount of Pt by producing mesoporous structures with larger surface areas. Such a facile design of mesoporous metals and alloys should greatly contribute to future applications, such as micro-sensors, micro-batteries, micro-bioactive materials, and miniaturized devices. Definitely, this work deserves to be awarded with a Doctor of Engineering degree.

July, 2012

審査員

(主査)	早稲田大学客員准教授	博士(工学) 早稲田大学	山内悠輔
	早稲田大学教授	工学博士 (早稲田大学)	逢坂哲彌
	早稲田大学教授	工学博士 (早稲田大学)	黒田一幸
	早稲田大学准教授	博士(工学) 早稲田大学	門間聰之
	早稲田大学客員教授	理学博士 (大阪大学)	板東義雄

(学外審査員) Bilkent University, Professor, PhD (Middle East Technical University), Ömer Dağ