Graduate School of Advanced Science and Engineering, Waseda University

博士論文審査報告書

論文題目
Surfactant-Assisted Solution-Phase Synthesis of Nanoporous Metal Particles with Various Architectures

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Metal nanoparticles with desired shape and morphology have attracted a great deal of attention, because of their widespread use in energy conversion/storage devices, sensors, and catalysts. To date, a diverse spectrum of metal nanoparticles, such as nanospheres, nanocubes, multipods, dendrites, nanofibers/nanowires, nanocages, nanotubes, nanostars, and porous nanoparticles has been successfully synthesized. Especially, a great deal of effort has been devoted to the synthesis and characterization of porous nanoparticles. The porous nanoparticles provide high surface area and a large number of edges and corners, which are important factors for catalytic applications. In spite of the recent significant advancements, complex and multistep procedures and/or high temperature and pressure conditions are required for the preparation of nanoporous metals, making these procedures non-economic for scale up. Hence, the development of a facile and economic method for high yield synthesis of nanoporous particles with hierarchical architectures is still a challenging issue to be solved. For this purpose, this thesis focuses on a direct chemical deposition approach in aqueous solution phases. A wide range of multifunctional nanoporous metals with different morphologies and compositions has been successfully synthesized by a facile wet-chemistry approach.

In Chapter 1, the previous synthetic procedures underlying the formation and development of nanoporous metals are presented with emphasis on the recent important progress. Key scientific issues on various fabrication methods are discussed as well. In addition, several potential applications of porous metals, especially in energy conversion/storage systems, are summarized.

In Chapters 2-5, a direct chemical method for the synthesis of dendritic nanoporous metals with different structures and compositions is developed. In Chapter 2, the template-less synthesis of nanoporous Au sponge by a rapid and one-step method at room temperature is reported. HAuCl₄ solution is mixed with sodium borohydride (SBH) solution and subsequently the mixtures are stirred for several minutes. The formation of 3D sponge structure during the reduction process is induced by kinetically controlled reduction of Au species. Since the SBH molecules release electrons by self-decomposition in the aqueous solutions, a large amount of hydrogen bubbles is generated during the Au deposition, forming the voids with different sizes in the products. This method demonstrates capability of scale-up with simple equipments, which is an important step for extending the solution phase synthesis to other nanoporous metal particles.

In Chapter 3, block copolymer-assisted synthesis of an Au metal core coated with a dendritic Pt shell (Au@Pt) by a rapid and efficient wet-chemical route is reported. For the preparation of Au@Pt nanospheres, ascorbic acid solution as a mild reducing agent is added to the precursor solution containing Au and Pt salts and Pluronic F127. Because of the different reduction potentials of Au and Pt
species, the reduction of Au ions preferentially occurs over a short time to form the Au seeds. It is followed by overgrowth of Pt nanodendritic shell on the Au seeds. The dissolved nonionic surfactant, Pluronic F127 serves as a structural-directing agent to form dendritic nanoporous structure. Thanks to effective increase of electrochemically active Pt surface areas, the Au@Pt nanocolloids can realize enhanced activity as an electrocatalyst for methanol oxidation reaction. This simple synthetic concept can open new avenue to create novel core-shell nanostructured metals, which will be significant finding with an aim to reduce the usage of Pt because of its limited resources and high cost.

In Chapter 4, the above method is further extended to synthesis of dendritic nanoporous bimetallic Pt-Ru alloy by replacing Ru precursor with Au precursor. Such a compositional modification of the Pt catalyst plays a key role in reducing CO poisoning and improving the activity. The obtained particles have well-defined dendritic nanoporous structures with randomly branched nanowires. Electrochemical experiments show high catalytic activity toward methanol oxidation reaction as well as drastic improvement in tolerance to CO poisoning. Thus, the approaches with low-concentrated surfactant solutions are widely applicable to other metal and alloy systems.

Chapter 5 describes synthesis of hollow Pt spheres with tunable dendritic shell thicknesses by using silica particles as templates. Silica particles are used as template to form the hollow interior, while nonionic surfactants assist to create the nanoporous dendritic Pt shell. Such a unique Pt nanostructure with hollow interiors effectively improves the electrocatalytic performance as Pt catalysts by facilitating access of electroactive species to the full-extent Pt surface. The essence of the present research is to exploit the advantages of both nanoporous and hollow structures.

Even though the dendritic nanoporous structures exhibited well-developed porosities and high surface areas, a network of very tortuous pores in particles slightly hampers the diffusion of reactants and products which are involved in catalytic reactions. Hence, the above methods described in Chapters 3-5 are further optimized to achieve hierarchical mesoporous structures with large pore size and open structure. In Chapters 6-7, new approach for synthesis of mesoporous materials with uniform pore sizes is proposed and developed. In this approach, coupling surface assembly of surfactants with slow chemical reduction of metal species can synthesize complicated mesoporous architectures with multifunctional properties.

In Chapter 6, a new class of hollow mesoporous Pt-Ru particles with a uniform size is presented. To realize the full potential of mesoporous metals as electro-catalysts, the shell thicknesses, compositions, and hollow cavity sizes can be precisely controlled by changing the reaction times, precursor compositions,
and silica particle sizes, respectively. Short diffusion pathway in thin mesoporous shells can greatly facilitate the diffusion of reactants and products and hence effectively increase the electrocatalytic activity of mesoporous cells. Such mesopores with uniform sizes exhibit superior electrocatalytic activity in comparison with other dendritic nanoporous samples.

In **Chapter 7**, synthesis of Pd@Pt nanocolloids with concave structure by one-step and efficient wet-chemical route is reported. The key important factors in the proposed method are self-assembly of surfactant micelles in the low concentrated surfactant solutions and precise control on the reduction rates by adding acid solutions to the precursor solutions. Because of the different reduction potentials of Pd and Pt species, the reduction of Pd ions preferentially occurs over a short time and followed by overgrowth of Pt on the Pd seeds. Thus, the use of surfactant assembly in aqueous solution phases leads to formation of interesting artificial mesopores and concave surfaces with uniform sizes.

**Chapter 8** describes general conclusions and prospective directions of the research which are nicely presented.

The present surfactant-assisted solution-phase synthesis can be extended to fabrication of many other metals and their alloys by designing appropriate precursor solutions. From another viewpoint, rational design of Pt-based nanostructures with desired composition will be useful to tackle challenging issues for commercialization of fuel cells such as short lifetime and low efficiency of catalysts. By applying this synthetic strategy to various kinds of templates, more complicated nanoarchitectures with multifunctional properties can be achieved straightforwardly in the future. Therefore, the developed approach in this thesis opens a new door toward new all-metal nanoporous materials. Definitely, this work deserves to be awarded with a Doctor of Engineering degree.

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