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

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Preface

Mesoporous metal particles have attracted much attention for years because of their beneficial uses as catalysts. The porous particles provide high surface area and a large number of edges and corners, which are important factors for catalytic applications. In spite of the recent advancements in synthesizing porous nanoparticles, complex and multistep procedures and/or high temperature and pressure conditions are required for the preparation of nanoporous metals. Hence, I focused on designing a straightforward solution phase approach for the high yield synthesis of nanoporous particles with uniform size and morphology. All the nanoporous structures were simply synthesized by purposefully changing the synthetic parameters including precursor composition (e.g. type and concentration of metal salts and surfactants, and pH) and synthetic conditions (e.g. synthetic temperature and ultrasonic irradiation). The effect of the synthetic conditions on the final morphology of products was carefully discussed. The formation of different structures and the quality of product were correlated with the nucleation and growth conditions. The correlations are explained in terms of surfactant micellization and reduction kinetics. I also demonstrated that a broad range of hierarchical nanostructures can be synthesized through a proper control on the synthetic parameters.

In Chapter 1, the previous synthetic procedures underlying the formation and development of nanoporous metal particles are presented with emphasis on the recent important progress. In Chapter 2, the template-less synthesis of nanoporous Au sponge by a rapid and one-step method is reported. In Chapter 3, block copolymer-assisted synthesis of a Au metal core coated with a dendritic Pt shell (Au@Pt) by a rapid and efficient wet-chemical route is demonstrated. In Chapter 4, the above method is extended to synthesize dendritic nanoporous Pt-Ru alloy nanoparticles. Chapter 5 describes a facile method to synthesize hollow Pt spheres with tunable dendritic shell thicknesses by using silica particles as templates. In Chapters 6-7, new approach for synthesis of mesoporous materials with uniform pore sizes is proposed and developed. In Chapter 6, a new class of hollow mesoporous Pt-Ru particles with a uniform size is presented. In Chapter 7, synthesis of Pd@Pt nanocolloids with concave structure by one-step and efficient wet-chemical route is reported. In Chapter 8, general conclusions and prospective directions of my research are presented.
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Chapter 1

1. General Introduction

1.1. Metal Nanoparticles

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 [1-4]. Metal nanoparticles showed unique physiochemical properties compared to their bulk counterparts. It has been experimentally and theoretically found that morphology and structure of nanoparticles strongly affect the physical and chemical properties of nanoparticles. Rational design of nanoparticles is therefore required to precisely tune the properties of the nanoparticles. Hence, by simply tuning the particle shape and morphology, we can create novel nanostructures with new physiochemical properties from the same materials. Another motivation for the rational design of nanoparticles is to investigate the effect of morphology on various properties of materials. On the other word, an ability to engineer materials on a nanometer length scale enables the investigation into the fundamental size- and shape-dependent properties of matter [4, 5]. To date, a diverse spectrum of metal nanoparticles, such as nanospheres [6], nanocubes [7-9], nanostars [10], nanodendrites [11-13], nanofibers/nanowires [14], nanocages [15], nanotubes [16], and porous nanoparticles [17] have been successfully synthesized (Please refer to Figure 1.1).
To prepare metal nanoparticles, solution phase strategies are generally adopted, in which a metal salt in aqueous or nonaqueous precursor solution is reduced by an appropriate reducing agent. Various colloidal strategies are applied to precisely control affecting parameters on the final morphology including the nucleation and growth process and/or dissolution and etching. Capping agents or stabilizers, such as surfactants and polymers are often added to prevent aggregation or enhance the chemical stability of the prepared nanoparticles because the high surface free energy of metal nanoparticles makes them sinter easily. [18-22].

Solution phase methods have some advantages over the other approaches which are as follows:
1) Simplicity of the procedure and required equipments;
2) Capability of scale up with simple equipments;
These reasons are critically important for using these materials in real applications such as energy conversion/storage devices, sensors, and catalysts [21, 22].

1.2. Nanoporous Metal Particles

Among all these metal nanoparticles, a great deal of effort has been devoted to the synthesis and characterization of porous particles. The porous particles provide high surface area and a large number of edges and corners, which are important factors for catalytic applications.

1.2.1. Soft and Hard Template Methods for Fabrication of Nanoporous Metals

Up to date, a wide range of mesoporous materials such as silica, carbon, inorganic-organic hybrids, polymers, and metals have been successfully prepared by various methods including hard template and soft template process. Among all these mesoporous materials, a great deal of effort has been devoted to the synthesis and characterization of mesoporous metals because of their unique electrocatalytic properties [23]. Nanoporous metals with high surface area have recently attracted growing interest because of their high potential as catalyst in the energy conversion devices. Both soft and hard templates can be generally employed for the synthesis of metallic porous structures.

1.2.1.1. Hard Template Method

In the hard-template method, deposition of mesoporous materials occurs in a confined space of template. Well defined mesoporous silica with desired structure has been commonly used as a hard template because of its robust framework and low cost (Please refer to Figure 1.2a) [23-26].
Figure 1.2. Synthetic procedure for the a) hard-template and b) soft-template process for the preparation of metal-based nanomaterials. The original figure is published in reference [23a].

Terasaki and co-workers [24] reported the synthesis of asymmetrically mesostructured platinum networks by using MCM-48 as hard template and H₂ as reducing agent. By coupling electrochemical deposition of Pd salt with hard template method, Lu and co workers [25] successfully synthesized a thin film consisting of ordered arrays of Pd nanowires. Very recently, Yamauchi and coworkers [26] extended hard template method for the synthesis of mesoporous metal nanoparticles with uniform shapes and sizes. Mesoporous Pt single crystals were synthesized through controlled chemical reduction and using mesoporous silica (KIT-6) as hard template (Please refer to Figure 1.3.a and b). Mesoporous Pt particles with polyhedral shape are prepared by slow reduction of Pt salts using ascorbic acid as a mild reducing agent.
1.2.1.2. Soft Template Method

After the first report on the successful preparation of mesoporous Pt particles by Attard and coworkers [27] in 1997, Soft templates composed of self assembled micelle structures, have been extensively used for producing nanoporous metals. In this method, the pore diameter and structure of mesoporous metals (i.e. lamellar, 2D hexagonal (p6mm), 3D cubic (Ia3d) and etc.) can be easily controlled by changing the composition of the LLCs. Well defined
mesoporous metals have been synthesized by chemical or electrochemical deposition of metal ions in lyotropic liquid crystals (LLCs) made of concentrated surfactant solutions (Please refer to Figure 1.2b) [27-32]. Recently, Yamauchi and Kuroda and coworkers [32] demonstrated the formation of novel mesoporous Pt with closely connected giant mesocages by using LLCs consisting of amphiphilic diblock copolymers (Please refer to Figure 1.3c and d).

In spite of the recent significant advancements of the template syntheses, because of the inflexibility and limitations of both common methods, they are mainly limited to producing simple structures such as nanoporous large particles with irregular shape and morphology. Because the morphology, size and size distribution of nanostructures are especially important for their function and role for particular applications, it is extremely important to prepare uniform-sized particles with the same shapes in high yields. To bring out shape- and size-dependent physicochemical properties, solution phase approach has received considerable attention in the fabrication of nanoporous metal particles [26, 31, 33].

1.2.2. Solution Phase Approach

Rational synthesis of porous metal particles with superior properties by solution phase methods has been significantly developed recently, and it is become possible to create nanoporous particles, for a wide spectrum of metals such as Pt, Pd, Au, Ag, and Rh [34-36]. It should be pointed out that even though early reports on the synthesis of nanoporous metal particles was based on experiments and observations, recent studies shed light on the mechanisms which are responsible for the formation of nanoporous particles. Understanding of nucleation and growth mechanisms of nanoporous metal particles will enable us to rational design hierarchical porous nanostructures with superior properties [34]. The nanoporous metal colloids, especially metals with dendritic morphology, are one of the most complicated structures which are possible to synthesize by solution phase routes. Because of their concavity which give them large surface area and high surface energy, the synthesis of such structures is thermodynamically unfavorable. Therefore they mainly synthesized via precise kinetic control [37]. The main solution phase methods are as follows:
1.2.2.1. Aggregation-Based Method

Synthesis of porous nanoparticles by aggregation-based method is mainly limited to the synthesis of Pt and Pd dendritic nanoparticles that involved the solution-phase reduction of platinum and Palladium salt precursors, such as Pd(acac)₂, H₂PtCl₆ and K₂PtCl₄, by a mild reducing agents (e.g. ascorbic acid and formic acid). In the most of these studies, a relative high reduction rate as well as polymeric stabilizer or surfactant such as poly vinyl pyrrolidone (PVP), Pluronic F127 block co-polymer, tetradecyl trimethyl ammonium bromide, or sodium dodecyl sulfate is critical for the successful synthesis of dendritic nanoparticles [34, 38-42].

Yamauchi and co-workers recently reported surfactant mediated synthesis of dendritic Pt nanoparticles with narrow size distribution and large surface area (Please refer to Figure 1.4) [40, 41, and 43]. Their studies demonstrated the important role of surfactants as structural-directing agent. The formation mechanism of dendritic Pt structure is explained by the formation of a crown-ethers-like conformation. The poly ethylene oxide (PEO) group in Pluronic surfactants (poly ethylene oxide-poly propylene oxide-poly ethylene oxide (PEO-PPO-PEO)) is known to form a crown-ethers-like conformation, similar to a cavity in the water-based solutions. Due to the interaction between the hydrophobic PPO groups and deposited Pt, the adsorbed surfactants on the surface of Pt can form cavities during reduction reaction and induce the dendritic structure [44, 45].
The formation mechanism of dendritic nanoparticles was further studied by Xia and co-workers and Skrabalak and co-workers with the synthesis of Pt and Pd nanodendrites, respectively. However, they suggested a new mechanism in which the formation of dendritic structure was attributed to the self-assembly of tiny metal seeds [46, 47]. In this new proposed approach, instantaneous nucleation of metals in a short time due to the high reduction rate of metal ions, lead to the rapid formation of large number of tiny seeds with high surface to volume ratio. In order to reduce the huge surface energy, these small seeds are self-assembled into dendritic particles [42] (Please refer to Figure 1.5a). It should be pointed out that the high mobility of tiny seeds in colloidal suspension also accelerates the coalescence of small metal particles [42, 47].
The attachment of metal seeds is guided by facet-specific capping agents. The energy barrier for coalescence on different facets depends on the capping tendency of surfactants for different crystallite facets. Such a facet-oriented attachment of tiny seeds by sharing a common crystallographic orientation leads to the formation of dendritic structure. Diffusion of metal atoms across the interface of attached crystallites aid the perfect merging of tiny crystallites [42]. However, some reports showed the polycrystalline structure of dendritic particles [40]. It can be attributed to the misorientation at the interface because of the twinning or imperfect coalescence of tiny seeds [34]. The morphology of final products greatly depends on the concentration of tiny seeds and their size and mobility in solution [42, 47]. In this method, the surfactant concentration can strongly affect the architecture of final products. When the concentration of surfactant in precursor solution is too low, there are not enough surfactants to cap the metal seeds and guide the random attachment. On the other hand, when the concentration of surfactant is higher than critical micelle concentration (CMC), the hydrophobic parts of the surfactants are hidden inside the micelles and do not have the capability of capping metal seeds [42].

Figure 1.5. Various pathways that can lead to porous nanoparticles: (a) aggregation-based growth into a nanodendrite; (b) aggregation based growth in the presence of a foreign nanocrystal seed and formation of a bimetallic nanodendrite. The original figure is published in reference [34].
1.2.2.2. Seeded Growth Method

In this approach, the surface of pre-formed metal seeds provides large number of nucleation sites for the overgrowth of another metal. This method has been used extensively for the rational design of metal nanoparticles for different applications [48]. Seeded growth also offers a simple and powerful approach for the preparation of Core–shell nanospheres with nanoporous metal shell. Tiny metal seeds formed in the solution can self assembled into dendritic structure on the pre-formed seeds. The attachment of tiny metal seeds can be guided by the different capping agents (Please refer to Figure 1.5b) [42]. Dendritic Au@Pt nanoparticles have been prepared by the deposition of a dense array of Pt nanowires on the Au pre-formed seeds in an organic precursor solution [49, 50]. Recently, Xia and co-workers have synthesized bimetallic core-shell nanospheres with Pd core and dendritic Pt shell by an aqueous route in which Pd nanocrystals were used as a seed to guide the growth of dendritic Pt shell. (Please refer to Figure 1.6) [34, 51]. Because of the small lattice mismatch between Pd and Pt, deposited Pt shell and Pd core showed epitaxial relationship at the interface (Please refer to Figure 1.6 b). Epitaxial growth of Pt on Pd was also demonstrated by Peng and Yang [52]. Recent studies shows that both homogeneous nucleation in solution and heterogeneous nucleation on Pd cores occur at the early stages of Pt deposition and is followed by the self-assembly of tiny Pt particles that had been formed by homogenous nucleation in the solution [46, 34].
Figure 1.6. (A) HRTEM image of Pd@Pt nanoparticle. (B) HRTEM image recorded from the center of the Pd@Pt nanodendrite shown in (A). The image clearly shows the continuous lattice fringes from the Pd core to the Pt branches, demonstrating the epitaxial relation between Pd and Pt. (C to F) HRTEM images recorded from Pt branches 1, 2, 4, and 6 marked in (A), respectively. The original figure is published in reference [51].

Recently, Yamauchi and co-workers proposed one step synthesis of double and triple-layered metallic core-shell colloids including Au@Pt, Pd@Pt and Au@Pd@Pt by co-reduction of metal ions [45, 53-55].

The Au@Pt core-shell nanocolloids with a Au core and a dendritic Pt shell were successfully synthesized by chemical co-reduction of H\textsubscript{2}PtCl\textsubscript{6} and HAuCl\textsubscript{4}, in the presence of Pluronic F127 with an ultrasonic treatment [45]. In this novel method, step-by-step reduction of metal ions spontaneously occurred in one step without any additional treatment. The difference in the reduction potential of different precursors plays a key role for the automatic phase separation. Interestingly, thickness of the porous Pt shell can be easily controlled by varying the molar ratio of the metal salts in the precursor solution. The optimization of the shell thickness led to the drastically improvement in the electrocatalytic activity of catalyst. The Pt-mass normalized activity of Au@Pt core-shell nanospheres toward methanol oxidation reaction was around 4 times larger than that of the dendritic Pt nanocolloids without the Au
cores [45]. This method is successfully extended to the synthesis of the triple-layered Au@Pd@Pt core-shell nanospheres consisting of Au core, Pd intermediate layer, and dendritic Pt outer shell. Through adding Pd intermediate layer to the Au@Pt structure, further enhancement of catalytic activity was obtained [42, 53-55].

Figure 1.7. (a) TEM image, (b) HAADF-STEM image and (c) HAADF-STEMEDS mapping images of the Au@Pd@Pt nanoparticles. (d) Cross-sectional compositional line profiles of the square area in Figure c. The original figure is published in reference [53].

It is worth pointing out that because the interaction of the pluronic F127 and Pt is stronger than that of F127 and Au or Pd, F127 can cap Pt tiny particles and form dendritic Pt structures while Au@Pd core is compact and did not show any porosity (Please refer to Figure 1.7) [53, 42].

It should be also pointed out that dendritic nanoparticles composed of numerous interconnected nanowires shows tortuous porosity while core-shell dendritic particles shows
an open structure and less overlap between neighboring branches (Please refer to Figure 1.8) [46, 51, 55].

![Figure 1.8](image)

Figure 1.8. (a) Highly magnified TEM image and (b) corresponding EDS mapping images of one Pd@Pt nanoparticle. The blue arrows in the inset of (a) indicate several atomic steps on the Pt branch surface. The original figure is published in reference [55].

The dendritic structure in both dendritic nanoparticles and core-shell nanoparticles is originated from the self assembly of tiny particles. The pre-formed metal cores strongly affect the self-assembly mechanism by providing isolated sites for the particle attachment to prevent overlap between the neighboring branches [34, 45, 46, 51, 55].

1.2.2.3. Galvanic Replacement

Galvanic replacement approach is an effective method for the synthesis of nanoparticles with nanoporous structure and hollow interior. The difference in the electrochemical reduction potentials between a sacrificial metallic template and noble metal ions plays a key role in this simple and versatile method. In this route, gradual oxidation and dissolution of the metallic
template is followed by reduction of less reactive metal ions and deposition of resulting atoms on the surface of metallic template [48].

The galvanic replacement between Ag seeds and Au metal ions can be used as a general example to understand the synthetic process. To avoid the precipitation of AgCl on the template surface, this reaction occurs in boiling water. Figure 1.9 shows a schematic image and the progress of the galvanic replacement reaction is monitored by the scanning electron microscopy (SEM) images at different stages of reaction between Ag nanocubes and HAuCl₄ [48]. In the early stage, after adding Au salt to the suspension of Ag nanocubes, a small hole formed at a defect site on the surface of the Ag template (Please refer to Figure 1.9C). While more Ag was dissolved, this small hole gradually expanded into the interior of the Ag template. Simultaneously, the outer surface of Ag template was protected from oxidation by deposited Au atoms on the surface. Released electrons at the Ag template can easily move to the cathode (outer surface of template) to reduce Au³⁺ ions. Figure 1.9D-F shows how this hole expanded to fill the entire particle and formed the hollow space inside the Ag template. Finally, expansion of this hole led to the formation of hollow nanoparticles (Please refer to Figure 1.9E). It should be pointed out that at this stage, the walls composed of an Au–Ag alloy, did not show any porosity because of the volume diffusion and dissolution and deposition process. After removing Ag from the Au-Ag alloy, a large number of vacancies were formed in hollow shell. Due to the incorporation of these vacancies and reconstruction shell into a structure with a lower surface area, hollow nanoboxes transformed into nanocages (Please refer to Figure 1.9G) [56, 57].
Figure 1.9. (A) Schematic image illustrating the major morphological and structural changes involved in the galvanic replacement reaction between a sharp Ag nanocube and HAuCl₄. The cross-sectional views correspond to the plane along the dashed lines. (B) SEM image of the sacrificial templates, Ag nanocubes; and (C–G) SEM images for the hollow nanostructures obtained from sequential stages of the galvanic replacement reaction. Insets of (D) and (E) are microtomed TEM samples showing the hollow interior, and insets of (B) and (F) are the electron diffraction patterns for the corresponding nanostructures. The 100 nm scale bar applies to all SEM images. The original figure is published in reference [56].

Up to know, nanoporous hollow spheres for various metals have been successfully synthesized by Galvanic displacement reactions between sacrificial metal templates (e. g. Co [58-61], Ag [56, 57, 62-65], and Pd [66]) and noble metal ions. It should be pointed out that the shape and size of the final product strongly depends on the size and morphology of the sacrificial templates and the extent of galvanic replacement [48].
1.3. Thesis Directions

Synthesis of nanoporous metal particles with desired shape and morphology has attracted a great deal of attention, because of their widespread use in energy conversion/storage devices, sensors, and catalysts. In spite of the recent significant advancements in synthesizing porous nanoparticles, 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. In addition, most of these methods have poor yield of a given morphology. In the case of mesoporous particles, synthetic approaches are mainly limited to producing simple structures such as nanoporous large particles with irregular morphologies. Hence, straightforward and facile synthesis of nanoporous metals is still challenging issue for the widespread use of them in industry.
1.4. References


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Chapter 2

2. Facile Synthesis of Nanoporous Au Particles

2.1. Introduction

In the recent years, metal-based nanoporous materials have attracted a great deal of attention because of their various applications in various fields including electrocatalysis, photochemistry, sensing, and biofiltration. Different techniques for the production of various nanoporous materials have been developed so far. Among them, templated syntheses have been regarded as a general concept for making nanopores in metals. For example, by using colloidal crystals or other aggregated nanoparticles as templates, nanoporous metals with various compositions can be produced. By applying electrochemical processes with colloidal crystal templates, well-ordered nanoporous Au, Pt, Ni, Co, and metal oxide films have been reported [1,2]. Amphiphilic molecules such as surfactants can be also used as soft templates [3-6]. Ordered mesoporous metals can be realized by chemical reduction of metal species in the presence of lyotropic liquid crystals made of highly concentrated surfactants [5]. As other approaches for the synthesis of nanoporous metals, biopolymer-assisted hydrothermal strategies [7] and dealloying [8-11] methods have been recently proposed. All of the previous methods, however, included complicated processes, and several steps and precise control of synthetic parameters such as pH and temperature are required.

In this chapter, I report templateless synthesis of nanoporous Au sponge by a rapid and one-step method at room temperature. Although very recently templateless synthesis using β-D-
glucose was reported, the 12-h reaction period is too long, which is a serious problem for large-scale production [12]. The present method was shown to have high yield (ca. 100%), rapid synthesis rate, low cost, and capability of scale-up with simple equipment.

Recent efforts have focused on the use of nanostructured Au as substrate for SERS [13, 14]. Our nanoporous Au sponge consisting of interconnected nanowires showed excellent activity as suitable substrate for SERS. Furthermore, the sponge will be an active catalyst for carbon monoxide and NO\textsubscript{x} oxidation in the future.

2.2. Synthesis of Au Nanoporous Particles

The starting precursor solutions were prepared by dissolving precise amounts of HAuCl\textsubscript{4} in water. The concentration of HAuCl\textsubscript{4} was varied from 1 to 20mM. For the preparation of nanoporous Au sponge, 5mL of HAuCl\textsubscript{4} solutions was mixed with 25mL of sodium borohydride solution (40 mM). The mixtures were stirred for several minutes. After finishing the reaction, the deposited Au particles were agglomerated. The amount of reducing agents was sufficient to completely reduce all the Au species. Therefore, the solution colors were changed to transparent clear.

2.3. Characterization of Au Nanoporous Particles

Figure 2.1a shows the low-magnified SEM image of the gold nanosponge prepared with 20mM HAuCl\textsubscript{4} solution. The obtained samples showed bulk morphology with larger than 200 μm in size. In the deposited particles, several voids of a few micrometer size were formed (Please refer to Figure 2.1).
Figure 2.1. SEM images of nanoporous Au sponges prepared by using 10mM HAuCl4 solution. Figure (b) is highly magnified SEM image. The morphology of samples was observed with a Hitachi S-4800 field emission scanning electron microscope (FE-SEM).

Since the reduction force of SBH is very strong, the SBH molecules released electrons by self decomposition in the aqueous solutions. Therefore, a large amount of bubble of hydrogen gas was generated during the Au deposition, forming the voids with different sizes in the products. Higher magnified SEM image in Figure 2.1b shows that the Au nanowires are interconnected to make the macropores. The Au nanowires had many branches and the nanowire size was in the range of 10 to 30 nm. Close observation of these networks showed that pore sizes were not uniform. Additionally, the high-angle XRD diffraction showed the several peaks corresponding to Au fcc structure (Please refer to Figure 2.2).
Generally, SBH molecules spontaneously release lots of electrons by self-decomposition, so that metal species are reduced into metal immediately. By taking advantage of self-decomposition of SBH at low pH in aqueous solution, SBH has been widely used for the formation of fine nanoparticles [15-17]. The formation of nanostructured metals is highly dependent on the concentrations of the dissolved metal species. With increase of the concentrations of the metal species, the fine nanostructures such as nanoparticles are not easily formed. The similar situation was observed in the present system. Figure 2.3 shows SEM images of the resultant products prepared under various concentrations of HAuCl₄ (The concentration of SBH was constant). As shown in Figure 2.3, well defined nanosponges with the same morphology could be successfully produced in the range from 1 to 20mM concentrations. However, when the concentration of the HAuCl₄ was over 200 mM, micron-sized Au particles without any porous network were deposited. When the concentration of the Au species was much higher, lots of Au nuclei were immediately generated and then were gathered to form bulk irregular particles.
Recently, Au and Ag nanoparticles have been utilized as substrate for SERS applications. Large SERS enhancements can be achieved at particle junctions of the particle aggregates. It was previously reported that the aggregated nanoparticles showed superior SERS activity than isolated individual nanoparticles [18]. Because our nanoporous Au sponges possesses sufficient particle junctions, it is expected that they show excellent SERS activity. To investigate the SERS, Rhodamine B was used as the probe molecule. Rhodamine B (1.0 μM) was immobilized on the nanoporous Au sponges by drop casting. As a reference, a flat Au substrate without any nanostructures was used. As shown in Figure 2.4, the intensities of the SERS signals in nanoporous Au sponge were dramatically increased, which is attributed to the surface enhancement effect of the Au sponges. The peaks were clearly associated with Rhodamine B [13].
2.4. Conclusion

In conclusion, we synthesized nanoporous Au sponges with high surface area by kinetically controlling the SBH reduction process. Our Au nanosponges will be good substrates for SERS applications. Also, our process can be simply extended to obtain nanosponges of other metals such as Ag, Pd, and Pt and alloys.
2.5. References


Chapter 3

3. Block Copolymer Assisted Synthesis of Bimetallic Colloids with Au Core and Dendritic Pt Shell

3.1. Introduction

Currently, nanoporous/mesoporous inorganic materials with high surface area have been prepared through a self-assembly process of surfactants [1-4], and they are expected to be utilized for many applications such as adsorbent materials and catalytic supports. Nanoporous materials with controlled compositions, different types of nanostructures, different pore sizes, and various morphologies have been extensively investigated during recent decades. Especially, the compositions strongly govern the materials’ properties. Recently, the possible compositions have been drastically extended to not only silica but also carbon, inorganic−organic hybrids, polymers, and even metals [5-10]. Nanoporous metals are considerably interesting, because we can expect huge electrochemical applications, such as methanol oxidation reaction and oxygen reduction reaction, which are not attainable by other compositions [10].

Among all of the metal compositions, especially Pt and Pt-based nanostructures with high surface area and desired utilization efficiency have attracted a great deal of attention, because
of their unique catalytic activities [11-16]. Because of the high cost of Pt, optimizing both the size and shape of Pt nanostructures is necessary to reduce Pt loading [17, 18]. To date, various Pt nanostructures, such as nanospheres [19], nanodendrites [20-23], nanofibers/nanowires [24, 25], nanocages [26], nanotubes [27], and nanosheets [28], have been successfully synthesized. Currently, bimetallic core–shell nanospheres with a Pt shell have been widely studied. In comparison to Pt alone, such core–shell nanostructures not only improve the utilization efficiency of catalysts, but also reduce Pt usage in catalysts [29-38]. However, in all of these cases, complex procedures including at least two steps for the preparation of core–shell nanostructures with a dendritic Pt shell are proposed. Also, high-temperature and high-pressure conditions sometimes are required. Hence, the development of a facile and economic method for the one-step synthesis of core–shell nanostructures with a high Pt surface area is a challenging issue to be solved urgently. Another problem with the previous studies is that the size of the core–shell nanoparticles is widely distributed [39], becoming impossible to finely control the Pt shell thicknesses on the cores. For the realization of extremely high diffusion of guest species from the outside, the Pt shell thicknesses should be effectively decreased. There is a reciprocal relationship between the Pt shell thicknesses and catalytic activity. Therefore, in the structure-sensitive electrocatalytic reactions, tailored core–shell nanoparticles with an ideal Pt shell thickness and narrow particle size distribution are especially vital [18, 31].

To overcome the above serious problems at the same time, here, I report a new synthetic route for bimetallic Au@Pt nanocolloids with a Au core and a dendritic Pt shell, by utilizing a surfactant-assisted process with an ultrasonic irradiation treatment. This synthetic approach enables the production of monodispersed Au@Pt nanocolloids in a wide range of the Pt precursor concentrations. It becomes possible to precisely control the Pt shell thicknesses on the Au cores. Through optimization of the Pt shell thicknesses, we can realize the highest utilization efficiency of the Pt, which is a very important finding for future design of a new type of electrocatalyst. Also, the distribution of the particle sizes is very narrow, and the effect of the ultrasonic irradiation on the particle size distribution is carefully discussed. I believe that our method is suitable for large-scale production of nanocatalysts, because it is a one-step, inexpensive method for the synthesis of uniform nanoparticles with high Pt surface area.
3.2. Synthesis of Au and Au@Pt Nanospheres

3.2.1. Materials

H₂PtCl₆ and HAuCl₄ as metal sources were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Ascorbic acid (AA), which was used as a reducing agent, was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Pluronic F127 (Mₜₙ = 12600) was obtained from Sigma.

3.2.2. Synthesis of Au@Pt Spheres

In a typical synthesis of Au@Pt nanocolloids (Pt/Au molar ratio = 1.0), 3.0 mL of H₂PtCl₆ solution (20 mM) and 3.0 mL of HAuCl₄ solution (20 mM) were mixed with Pluronic F127 (0.06 g) in a small beaker. After that, 6.0 mL of AA solution (0.1 M) was added, and the mixture was then sonicated for 15 min. For a better understanding of the ultrasonic irradiation effect, in another experiment, the precursor solution after adding AA was mixed, using a magnetic stirrer, without the use of the ultrasonic treatment. After the reaction for 24 h, all the dissolved metal sources were completely deposited. The product was collected by centrifugation at 10000 rpm for 20 min and residual Pluronic F127 was removed by three consecutive washing/centrifugation cycles with acetone and water. The collected product was dried at 45 °C for several days. For further characterization, the dried product was redispersed in water to produce a stable colloidal suspension.

For the preparation of the Au@Pt nanocolloids with different Pt shell thicknesses, Pt/Au molar ratios in the starting solution were varied from 0.0 to 4.0. The added amount of HAuCl₄ (20 mM) was fixed to 3 mL, while the added amount of H₂PtCl₆ (20 mM) was changed from 0.0 mL to 12.0 mL. The molar ratios of the added AA and F127 to the dissolved metal species were fixed. The compositional ratios in the starting solution are listed in Table 3.1
Table 3.1. Compositional Ratios in Starting Solution

<table>
<thead>
<tr>
<th>sample</th>
<th>volume of H₂PtCl₆ solution (20 mM)</th>
<th>volume of HAuCl₄ solution (20 mM)</th>
<th>amount of F127</th>
<th>volume of AA solution (0.1 M)</th>
<th>Pt/Au molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0 mL</td>
<td>3.0 mL</td>
<td>0.03 g</td>
<td>3.0 mL</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>1.0 mL</td>
<td>3.0 mL</td>
<td>0.04 g</td>
<td>4.0 mL</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>2.0 mL</td>
<td>3.0 mL</td>
<td>0.05 g</td>
<td>5.0 mL</td>
<td>0.67</td>
</tr>
<tr>
<td>4</td>
<td>3.0 mL</td>
<td>3.0 mL</td>
<td>0.06 g</td>
<td>6.0 mL</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>6.0 mL</td>
<td>3.0 mL</td>
<td>0.09 g</td>
<td>9.0 mL</td>
<td>2.0</td>
</tr>
<tr>
<td>6</td>
<td>9.0 mL</td>
<td>3.0 mL</td>
<td>0.12 g</td>
<td>12 mL</td>
<td>3.0</td>
</tr>
<tr>
<td>7</td>
<td>12 mL</td>
<td>3.0 mL</td>
<td>0.15 g</td>
<td>15 mL</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The dendritic Pt nanocolloids without Au cores were prepared as follows. Three milliliters (3.0 mL) of H₂PtCl₆ solution (20 mM), containing 0.03 g of F127, was mixed with 3.0 mL of AA solution (0.1 M) and the mixture was sonicated for 15 min. After the reaction for 24 h, all the dissolved metal sources were completely deposited. The product was collected by centrifugation at 10000 rpm for 20 min and residual Pluronic F127 was removed by three consecutive washing/centrifugation cycles with acetone and water. The collected product was dried at 45 °C for several days.

3.2.3. Characterization

Transmission electron microscopy (TEM) observation was performed using a JEOL Model JEM-2100F TEM system that was operated at 200 kV and equipped for energy-dispersive spectrometer (EDS) analysis. The sample for TEM characterization was prepared by depositing a drop of dilute suspensions on a carbon-coated copper grid and the sample was dried at room temperature. Wide-angle powder X-ray diffraction (XRD) patterns were obtained with a Rigaku Model Rint 2500X diffractometer that was using monochromated Cu Kα radiation (40 kV, 100 mA) and was operated using a step scan program (step width = 0.05°). Nitrogen adsorption−desorption data was obtained using a Belsorp 28 apparatus (Bel Japan, Inc.) at 77 K. Ultraviolet−visible light (UV−vis) absorption spectra were recorded using a JASCO Model V-570 UV-vis-NIR spectrometer.

3.2.4. Electrochemical Measurements

Cyclic voltammogram (CV) experiments were performed using a CHI 842B electrochemical analyzer (CHI Instruments, USA). A conventional three-electrode cell was used, including an
Ag/AgCl (saturated KCl) electrode as a reference electrode, a platinum wire as a counter electrode, and a modified glassy carbon electrode (GCE) (3 mm in diameter) as a working electrode. The modified GCE was coated with as-produced Au, Au@Pt, and Pt nanocolloids (4.0 μg) respectively. Then, they were dried at room temperature. Prior to electrochemical experiments, the electrodes with Au@Pt and Pt nanocolloids were cleaned electrochemically by cycling the electrode potential between −0.2 V and +1.6 V (vs Ag/AgCl) in 0.5 M H₂SO₄ until CVs that were characteristic for a clean Pt electrode were obtained. Methanol electro-oxidation measurements were performed in a solution of 0.5 M H₂SO₄ that contained 0.5 M methanol at a scan rate of 50 mV/s.

3.3. Characterization of Au@Pt Nanocolloids

Figure 3.1 shows TEM images of the Au@Pt nanocolloids synthesized by ultrasonic-assisted method under the typical condition (the Pt/Au molar ratio used was 1.0). The lower-magnification image (Please refer to Figure 3.1a) indicates that the Au@Pt nanocolloids are strikingly uniform in morphology. The particle sizes were distributed in the range of 20−35 nm. No other isolated Pt or Au nanostructures were observed, demonstrating the high yield (100%) synthesis of the Au@Pt nanocolloids. In all of the nanocolloids, a dark center was surrounded by a gray dendritic shell. This strong contrast revealed the formation of a core–shell structure (Please refer to Figure 3.1a and b).
Figure 3.1. (a) Low-magnification and (b) high-magnification TEM images of Au@Pt nanocolloids prepared from a typical solution with a Pt/Au molar ratio of 1.0. (c) High-magnification TEM image of the Pt shell. (d) Selected-area electron diffraction (SAED) patterns taken from the Pt shell region.

For further characterization of Au@Pt nanocolloids, high-resolution transmission electron microscopy (HRTEM) was applied to investigate the nanostructure and the lattice of an individual Pt shell (Please refer to Figure 3.1c). The overgrowth of Pt dendritic nanowires on the Au core could be seen in the high-magnification TEM image. The Pt dendritic shells were composed of many interconnected nanowires 3 nm in diameter. The observed lattice fringes corresponded to the (111) planes of Pt face-centered cubic (fcc) crystals and they were randomly oriented over the entire area (Please refer to Figure 3.1c). Selected-area electron diffraction (SAED) patterns of the Pt shells showed the ring patterns with intense spots assigned to (111), (200), (220), and (311) planes of Pt fcc crystals, showing the polycrystalline nature of Pt (Please refer to Figure 3.1d). The elemental mapping as well as the line scanning
also showed that the center of the particle is pure Au, whereas Pt is concentrated at the outer edge of the particle (Please refer to Figure 3.2).

Figure 3.2. (a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Au@Pt nanocolloids prepared from a typical solution with a Pt/Au molar ratio of 1.0. (b) Elemental line scanning over the entire particle region indicated by the red line in panel (a). (c) Elemental mapping of the Au@Pt nanocolloids prepared from a typical solution with a Pt/Au molar ratio of 1.0. In panels (b) and (c), the red color indicates Au, whereas the blue color indicates Pt.

From the corresponding elemental mapping data, it was revealed that Pt and Au were distributed according to the morphology of the Au@Pt core–shell nanocolloids (Please refer to Figure 3.2c). This is direct evidence of the formation of an Au@Pt core–shell structure. The wide-angle XRD patterns of the Au@Pt core–shell nanocolloids showed both Au fcc and Pt fcc peaks, indicating the nonalloy structure (Please refer to Figure 3.3).
The essence of the synthesis of Au@Pt core–shell nanocolloids is to exploit the difference in standard reduction potentials of the two metal salts (H$_2$PtCl$_6$ and HAuCl$_4$). In the present system, AuCl$_4^-$ and [PtCl$_6$]$^{2-}$ could be reduced according to the following reactions:

\[
\text{AuCl}_4^- + 3e^- \rightarrow \text{Au} + 4\text{Cl}^- \quad + 1.00 \text{ V vs SHE} \quad (7.1)
\]

\[
[\text{PtCl}_6]^{2-} + 2e^- \rightarrow [\text{PtCl}_4]^{2-} + 2\text{Cl}^- \quad + 0.68 \text{ V vs SHE} \quad (7.2)
\]

\[
[\text{PtCl}_4]^{2-} + 2e^- \rightarrow \text{Pt} + 4\text{Cl}^- \quad + 0.76 \text{ V vs SHE} \quad (7.3)
\]

The difference in the reduction potentials of the two soluble metal salts plays a key role in the one-step synthesis of a core–shell structure. Because of the large different reduction potential, the reduction of Au ions preferentially occurs in a short time to produce Au cores. This is followed by overgrowth of the Pt dendritic nanowires on the Au seeds. During the Pt deposition, the Pluronic F127 plays an important role as a structural-directing agent [21, 23]. On the other hand, during the formation of the Au cores, the F127 cannot act as a structural-directing agent. Actually, the Au cores in the Au@Pt possess no nanostructures (Please refer to Figures 3.1a and 3.1b). During the synthesis of the Au@Pt core–shell nanocolloids, I could
easily monitor the progress of the synthesis through the evolution of the solution color. The color of the initial solution containing Au and Pt ions and F127 was yellow. As shown in Figure 3.4, after adding ascorbic acid (AA) solution and applying ultrasonic irradiation, the color gradually changed to burgundy, indicating that only the Au species were preferentially reduced to Au nanoparticles (Please refer to Figure 3.4a). During the following 24 h, the solution gradually turned dark black, which is caused by growth of the Pt shells on the Au cores.

![Figure 3.4. Photographs of colloidal suspensions taken at different reaction times: (a) 1 h, (b) 3 h, (c) 6 h, (d) 24 h, and (e) 48 h. After reaction for 24 h, the colors of the colloidal suspensions are not changed. The Pt/Au molar ratio used in the starting solution is 1.0.](image)

Figure 3.4. Photographs of colloidal suspensions taken at different reaction times: (a) 1 h, (b) 3 h, (c) 6 h, (d) 24 h, and (e) 48 h. After reaction for 24 h, the colors of the colloidal suspensions are not changed. The Pt/Au molar ratio used in the starting solution is 1.0.

To further elucidate the synthesis progress, different stages of the formation of Au@Pt nanocolloids were observed by TEM (Please refer to Figure 3.5). As shown in Figure 3.5a, spherical Au nanoparticles were formed after 1 h reaction. Enough nucleation sites for reduction of Pt ions are provided by the surface of the Au seeds. Gradual reduction of the Pt species led to the continuous nucleation and growth of Pt nanowires on the Au seed. After the formation of primary nanowires, secondary Pt nanowires grew on Au seeds and the primary Pt nanowires (Please refer to Figure 3.5b), resulting in the formation of the dendritic Pt shell. The 6 h reaction was not sufficient to completely coat the Pt dendritic shell over the entire Au surface. In some parts, the exposed Au surface without the Pt shell was observed, as indicated
by the arrow in Figure 3.5b. The growth of Pt shell continued until the complete consumption of Pt ions in solution (Please refer to Figure 3.5c). At that time, the color of the solution changed to black (Figure 3.4). After a period of 24 h following the start of the reaction, the growth of the Pt dendritic shell was terminated and the product morphology was not changed anymore (Please refer to Figure 3.5d and 5e).

![Figure 3.5](image)

Figure 3.5. TEM images of samples taken at different reaction times: (a) 1 h, (b) 6 h, (c) 24 h, (d) 48 h, and (e) 72 h. After the reaction has proceeded for 24 h, the morphology of the Au@Pt nanocolloids is not varied at all. The Pt/Au molar ratio used in the starting solution is 1.0. The position of the exposed Au surface without the Pt shell is indicated by the arrow.

The synthesis progress could be visibly monitored by UV−vis absorption spectroscopy at different reaction times (Please refer to Figure 3.6). The solution after 1 h of reaction showed an extinction peak centered at 520 nm, originating from the Au surface plasmon (Please refer to Figure 3.6a and 3.6b) [40]. As the Au seeds were covered with the dendritic Pt shell, the absorption peak gradually shifted to longer wavelengths (Please refer to Figure 3.6c−e). This
red shift was accompanied by the suppression of the absorption peak, which was due to the formation of the dendritic Pt shell. These results confirmed a continuous overgrowth of the dendritic Pt shell on the surface of Au seed, which is consistent with TEM analysis (Please refer to Figure 3.5). After the reaction for 24 h, the shape of the peaks was not changed at all, indicating that the reduction reaction of the metal species was terminated within 24 h.

Figure 3.6. UV−vis absorption spectra of Au@Pt nanocolloids taken at different reaction times: (a) 30 min, (b) 1 h, (c) 3 h, (d) 6 h, (e) 24 h, (f) 48 h, and (g) 72 h. After 24 h of reaction, the shape of the peaks is not changed. The Pt/Au molar ratio used in the starting solution is 1.0.

To examine the effect of ultrasonic treatment and different Pt/Au molar ratios in the solution, two series of experiments were performed. In one experiment, the precursor solutions with various molar ratios of Pt/Au (in the range of 0.00−4.00) were sonicated for 15 min in the presence of F127 and AA (Please refer to Figure 3.7).
Figure 3.7. TEM images of (a) Au nanocolloids and (b–g) Au@Pt nanocolloids prepared by sonochemical reaction, using solutions with different Pt/Au molar ratios. The Pt/Au molar ratios are (a) 0.00, (b) 0.33, (c) 0.67, (d) 1.00, (e) 2.00, (f) 3.00, and (g) 4.00. The Pt nanodendrite without Au cores (as byproduct) is indicated by the dotted circle in panel (g).

In another experiment, the ultrasonic treatment was replaced by mixing of the precursor solution with a magnetic stirrer (Please refer to Figure 3.8). Inductively coupled plasma (ICP) analysis showed that, in all of the samples, the composition of the Au@Pt nanocolloids was stoichiometrically consistent with the Pt/Au molar ratios in the starting solution, indicating that the amount of AA as a reducing agent is sufficient to completely reduce all of the Pt and Au species.
Figure 3.8. TEM images of (a) Au nanocolloids and (b–g) Au@Pt nanocolloids prepared via a stirring process, using solutions with different Pt/Au molar ratios. The Pt/Au molar ratios are (a) 0.00, (b) 0.33, (c) 0.67, (d) 1.00, (e) 2.00, (f) 3.00, and (g) 4.00. The Pt nanodendrite without Au cores (as byproduct) is indicated by a dotted circle in panels (e), (f), and (g).

Figures 3.7 and 3.8 show TEM images of the Au@Pt nanocolloids synthesized by sonochemical reaction and using a stirring mixture, respectively. The Au@Pt nanocolloids prepared via sonochemical reaction had a smaller particle size with a narrow distribution, compared to those prepared by stirring mixture. The particle size distributions of the Au@Pt nanocolloids were investigated by counting more than 200 samples. As shown in Figure 3.9, the average size of the nanocolloids synthesized using the stirring mixture was 56 nm, with sizes ranging from 45 nm to 75 nm. In contrast, the size distribution of the nanocolloids prepared by sonochemical reaction was 20–35 nm, with an average size of 27 nm. By application of the ultrasonic irradiation, the average sizes were dramatically reduced and the particle size distribution became quite narrow.
As mentioned previously (Figures 3.5 and 3.6), primary Au seeds play the role of nucleation centers for growth of the Pt shell. The size and distribution of the final Au@Pt nanocolloids are dependent on those of Au seeds. Hence, the formation of Au cores with uniform size is necessary to create Au@Pt nanospheres with a narrow size distribution. The mechanism of the reduction of metal salts [41-43], especially HAuCl₄ [44], could be generally explained by a model including a slow progressive nucleation and fast autocatalytic growth. The particle size and the width of the size distribution of the Au particles are inversely related to the number of the Au nuclei, which corresponds to the rate of nucleation [45, 46]. In other words, when the number of the Au nuclei is smaller, the particle size has a tendency to increase and the size distribution broadens. This model can be adopted to explain the formation of Au seeds. In the mixture process that uses a magnetic stirrer, in the early stages of the reaction, Au seeds were slowly formed and served as nucleation centers. As the reduction reaction progressed, the formation of new seeds, combined with the autocatalytic growth of primary seeds, led to broadening of the particle size distribution. Finally, Au particle concentration reached a critical nucleus concentration and further seed formation was suppressed. Hence, the growth of Au predominates over the nucleation. In contrast, in the case of sonochemical reaction, the
rate of Au reduction is significantly accelerated by the ultrasound radiation. Hence, instead of progressive nucleation during the reaction time, instantaneous nucleation occurs within a very short time. This means that the ratio of Au seeds to metal ions is dramatically increased, and a critical nucleus concentration is reached rapidly and further seeding is suppressed. Thus, small-sized Au nanoparticles with a narrow size distribution could be obtained. Recently, the use of high-intensity ultrasonics for the preparation of metal nanoparticles has been established by theoretical and experimental studies [47-50]. The ultrasonic-induced reduction is a result of acoustic cavitation, which involves the formation, growth, and implosive collapse of vacuum bubbles in solution. Within a collapsing bubble, the generation of transient high temperatures and pressures leads to a hemolytic dissociation of water and other species to form reducing radicals [51]. Ultrasonic irradiation also provides not only high shear and stirring power but also homogeneous distribution of the mixing energy within the reaction volume without scale-up limitations. Consequently, instantaneous nucleation and homogeneous growth is induced by rapid reduction of the metal ions [52, 53]. In the present sonochemical method, Au seeds with uniform size serve as nucleation centers for Pt sources, with the result that Au@Pt nanocolloids with uniform sizes were finally obtained.

Interestingly, the thicknesses of the Pt shell were easily tuned by varying the molar ratio of Pt/Au in the initial solutions (Please refer to Figure 3.10). The shell thicknesses of the prepared Au@Pt nanocolloids were measured from TEM images. In the experimental, the amounts of added Au solution were fixed to be 3.0 mL, whereas only the amounts of added Pt solutions were varied from 0 mL to 12 mL (Please refer to Table 3.1). When the amount of Pt source was very small (1.0 mL) (i.e., the Pt/Au molar ratio is 0.33), several nanowires/nanoparticles with an average diameter of 2 nm grew up to a few nanometers and were sparsely distributed on the Au cores. The Pt dendrites did not continuously cover the Au cores (Please refer to Figure 3.7b). With the increase of the Pt/Au molar ratios, the average thicknesses of the Pt shell were proportionally increased (Please refer to Figure 3.10).
Figure 3.10. Relationship between the average Pt shell thicknesses and the added amount of Pt solutions. Au@Pt nanocolloids prepared by (a) sonochemical reaction and (b) stirring the mixture are compared. The Pt/Au molar ratios in the starting solutions are noted in parentheses.

In the case of stirring the mixture, when the Pt/Au molar ratio in the initial solution was further increased to 2.0, dendritic Pt particles without Au cores were confirmed as a byproduct in the TEM images (Please refer to Figure 3.8e). For Pt/Au molar ratios of more than 2.0, the amount of the byproduct was increased gradually as Pt/Au molar ratios were increased. However, in the case of the sonochemical reaction, no byproducts were observed until the Pt/Au molar ratio reached 4.00. This is because the size of the Au cores was decreased by the application of the ultrasonic irradiation (Please refer to Figure 3.7a and 3.8a), providing a larger Au exposed surface to volume.

The successful coating of the dendritic Pt shell on the Au core was characterized by UV−vis spectroscopy. Figure 3.11 shows the spectra of the Au@Pt nanocolloids from various solutions with different Pt/Au molar ratios. The Au nanocolloids without a Pt shell clearly showed an absorption peak centered at 520 nm, which was due to the surface plasmon resonance of Au nanocolloids (Please refer to Figure 3.11a). For Au@Pt nanocolloids with a Pt/Au molar ratio of 1.0, suppression and red shift of the absorption peak could be easily observed, because of overgrowth of the dendritic Pt shell. For higher Pt/Au molar ratios, the absorption peaks gradually diminish, because of the increasing Pt shell thickness [38].
Figure 3.11. UV–vis absorption spectra of (a) Au nanocolloids and (b–e) Au@Pt nanocolloids prepared by sonochemical reaction, using the solutions with different Pt/Au molar ratios. The Pt/Au molar ratios are (a) 0.00, (b) 1.00, (c) 2.00, (d) 3.00, and (e) 4.00.

To demonstrate their potential uses as metal catalysts, the surface area of the Au@Pt nanocolloids was measured using N$_2$ adsorption–desorption isotherms (Please refer to Figure 3.12). The specific surface of the typical Au@Pt nanocolloids was 34 m$^2$/g, a value that is very close value to that of the dendritic Pt nanocolloids (32.9 m$^2$/g). Based on the Pt-mass normalization, the specific surface area of the Au@Pt nanocolloids was roughly calculated to be 68 (m$^2$/g$_{Pt}$), which is approximately twice as large as that of the dendritic Pt nanocolloids.
Figure 3.12. N2 adsorption isotherms of (a) Au@Pt nanocolloids and (b) Pt dendritic nanocolloids prepared by sonochemical reaction. The Au@Pt nanocolloids are prepared from a typical solution with a Pt/Au molar ratio of 1.0.

3.4. Electrocatalytic Ability of Au@Pt Nanocolloids

As a preliminary demonstration of the electrocatalytic ability of Au@Pt nanocolloids, the electrocatalytic activity toward the methanol oxidation reaction was tested using the CV method in 0.5 M H₂SO₄ + 0.5 M methanol solution (Please refer to Figure 3.13). The current densities were normalized by the loading amount of the Pt. The Au nanoparticles without the Pt shells as a reference had no catalytic activity toward the oxidation of methanol. The Pt-mass-normalized activity of Au@Pt nanocolloids with Pt/Au molar ratios of 0.5 and 1.0 exhibited superior catalytic activity. These values were 85.8 and 116 mA/mg, respectively. However, with the further increase of Pt/Au molar ratios, the catalytic activity of Au@Pt nanocolloids is dramatically decreased. The Pt-mass normalized activity for the Au@Pt nanocolloids of Pt/Au molar ratios of 2.0 and 3.0 was 34.8 and 29.3 mA/mg, respectively. Consequently, the optimum Pt/Au molar ratio was determined to be 1.0. The obtained maximum electrocatalytic activity is around 4 times as large as that of the dendritic Pt nanoparticle without Au cores (28.5 mA/mg). The merit in the core–shell structures is the
possibility of coating electrochemically active Pt thin layers. The efficiency of an
electrocatalytic reaction is strongly dependent on the accessibility of the reactants to the
catalysts [38, 54]. In the Au@Pt nanocolloids with higher Pt/Au molar ratio or without a Au
core, the methanol electrolyte cannot gain access to inner parts of the thick Pt shell. In other
words, all of the Pt surface cannot work well as an electroactive surface. The enhancement of
the catalytic activity is expected through the optimization of both the shell thicknesses and
dimensions of the dendritic Pt layers.

![Cyclic Voltammograms (CVs)](image)

Figure 3.13. Pt-mass-normalized cyclic voltammograms (CVs) displaying the catalyzed
oxidation of methanol, using (a) Au nanocolloids, (b−d) Au@Pt nanocolloids, and (e) Pt
dendritic nanocolloids. The Au@Pt nanocolloids are prepared by sonochemical reaction using
the solutions with different Pt/Au molar ratios of (b) 0.33 (c) 1.0, and (d) 2.0.

3.5. Conclusion

The Au@Pt core–shell nanocolloids were successfully synthesized by chemical reduction of
H₂PtCl₆ and HAuCl₄ salts under an aqueous low-concentration surfactant solution. Via the
application of ultrasonic irradiation, the size of the Au@Pt nanocolloids was decreased and
their particle size distribution became narrow, compared with the Au@Pt nanocolloids
synthesized by stirring the mixture. Furthermore, the Pt dendritic shell thicknesses could be controlled by changing the Pt/Au molar ratios in the starting solutions. Through the careful optimization of the Pt shell thicknesses, the Pt-mass-normalized activity as an electrocatalyst for methanol oxidation reaction was drastically enhanced, which is around 4 times as large as that of the dendritic Pt nanocolloids without the Au cores. This is an important finding to improve the utilization efficiency of Pt catalysts in the future. The proposed method is a high-yield and low-cost pathway for metal-based core–shell structures, which have a large capability for scaleup.

Currently, inorganic core–shell structures have attracted interest as extensive research for integration of functionalities of both cores and shells [55-59]. Nanoporous/nanostructured materials with high surface areas have gained much attention as a promising candidate as shell materials [55-60]. However, the shell compositions have been mainly limited to nanoporous/nanostructured silica and carbon. In this chapter, I focused on metal-based core–shell structures with multifunctional architectures. This work can open new doors to creating novel metal-based core–shell structured materials with functional plasmonic, magnetic, and catalytic properties in the future.
3.6. References


Chapter 4

4. Facile Synthesis of Nanoporous Pt-Ru Alloy Nanospheres with Various Compositions

4.1. Introduction

Recently, numerous studies have focused on identifying new Pt-based catalysts that would meet all necessary requirements for their widespread use in fuel cells, such as high efficiency, durability, low cost, and capability of scale up. As the catalytic activity strongly depends on the structure and composition of the catalyst, much effort has been devoted to modify these characteristics to develop improved Pt-based catalysts [1–3]. Among these main strategies, the effect of the structure on the electrochemical activity of a catalyst has been well recognized [4–7]. The functionality of a catalyst is related to its surface; in other words, a catalytic reaction is a surface phenomenon and can occur only after the adsorption of reactant onto the catalyst surface [5]. Therefore, producing nanostructures with large surface-to-volume ratios can dramatically improve catalytic activity [6, 8]. In addition, Pt nanostructures with more edges and corners have been shown to possess higher catalytic activity [9]. Hence, the activity of electrocatalysts can be affected by manipulating the shape and morphology of catalysts. In this regard, up to date, many Pt-based nanocatalysts with various structures including nanocubes [10–12], nanospheres [13], nanodendrites [6,14–15], nanofibers/nanowires [16], hollow nanostructures [3, 17], nanotubes [18], and nanosheets [19], all of which were designed to maximize their active surface area, have been reported.
On the other hand, considerable effort has been devoted to improve catalytic properties of Pt catalysts by alloying with other elements (e.g., Ru, Pd, and Ni) [20–24]. Such a compositional modification of the Pt catalyst plays a key role in reducing CO poisoning and improving its activity. Among all of these alloys, the Pt–Ru catalyst is the most advantageous pertaining to catalytic activity and CO tolerance in the oxidation reaction of methanol [21, 25–26]. The improved electrochemical properties can be partially attributed to the bifunctional effect of Ru. According to the Langmuir–Hinshelwood mechanism, the adsorption of oxygen-containing species on Ru atoms facilitates the electrochemical oxidation of adsorbed CO on neighboring Pt to CO₂, which is essential for sustained catalytic activity [21, 26, 27–31]. In addition, electronic modification of Pt atoms by neighboring Ru atoms leads to weakening of the bond strength between Pt and adsorbed CO [32–34].

Although recent studies have achieved great improvements in the electrochemical activity and durability of catalysts, facile methods that combine both structural and compositional modifications are still lacking. To the best of our knowledge, up to date, only one method has been proposed for the synthesis of Pt–Ru alloy nanoparticles with dendritic structure in which reductant and precursor mixtures were prepared in two separate chambers and heated to 130 °C and 190 °C, respectively [26]. The reductant solution was subsequently injected into precursor mixture, heated to 280 °C, and maintained at this temperature for 30 minutes. The multistep procedures as well as high-pressure and high-temperature conditions are, however, disadvantageous for commercial use and large-scale production.

4.2. Experimental Section

4.2.1. Materials

H₂PtCl₆ and RuCl₃ (as metal sources) and ascorbic acid (as reducing agent) were obtained from Nacalai Tesque, Inc. (Kyoto, Japan). Pluronic F127 (Mw=12600) was purchased from Sigma. Commercial Pt black (HiSPEC® 1000) was supplied by Johnson Matthey Company.
4.2.2. Synthesis of Nanoporous Pt-Ru Spheres

In a typical synthesis of Pt-Ru nanospheres, 3.0 mL of $\text{H}_2\text{PtCl}_6$ solution (20 mM) was mixed with 2.0 mL of RuCl$_3$ solution (20 mM) in a beaker. Then, 50 mg of Pluronic F127 was dissolved in precursor solution. After adding 5.0 mL of AA solution (0.1 M), the mixture was sonicated for 40 min. The obtained black suspension was placed for 24 h at room temperature in order to provide more time for reduction of metal ions. Final product was collected by centrifugation at 9000 rpm for 15 min and residual Pluronic F127 and reductant was removed by five consecutive washing/centrifugation cycles with acetone and water. The collected product was dried at room temperature for several days.

4.2.3. Characterization

Transmission electron microscopy (TEM) observation was done at the electron acceleration voltage of 200 kV using a JEOL Model JEM-2100F TEM system equipped with an energy-dispersive spectrometer (EDS) for elemental analysis. For TEM sample preparation, the dried product was dispersed in water to produce a stable colloidal suspension. The small amount of the dilute suspension was dropped onto a carbon-coated copper grid and was dried at room temperature. Wide-angle X-ray diffraction (XRD) patterns were measured by a Rigaku Model Rint 2500X diffractometer with monochromated Cu Kα radiation (40 kV, 100 mA) at a scanning rate of 0.5° min$^{-1}$. Slow scanning XRD of the (311) peak was recorded in the 2θ range of 80 to 84° at a scanning rate of 0.05° min$^{-1}$. Nitrogen adsorption-desorption measurements were carried out by a Belsorp 28 apparatus (Bel Japan, Inc.) at 77 K and the surface area was measured with the Brunauer-Emmett-Teller (BET) method. XPS analysis was performed by using the spectrometer PHI Quantera SXM (ULVAC-PHI, Japan) with a monochromatic Al Kα X-ray source (50 W). The amount of Pt and Ru in each resulting sample was also determined by an inductively coupled plasma (ICP) spectrometer (IRIS Advantage, Nippon Jarrell-Ash).
4.2.4. Electrochemical Measurements

Cyclic voltammograms (CVs) experiments were performed by using a CHI 842B electrochemical analyzer (CHI Instrument, USA). A conventional three-electrode cell was used, including an Ag/AgCl (saturated KCl) electrode as reference electrode, a platinum wire as counter electrode, and a modified glassy carbon electrode (GCE) (3 mm in diameter) as working electrode. The modified GCE was coated with Pt-Ru or Pt samples with the same metal loadings of 3 μg. Then 3μl of 0.5 wt. % nafion solution was dropped on the surface of the electrode and the electrode was dried at room temperature. Prior to electrochemical experiments, The as-prepared electrode was electrochemically cleaned by cycling the electrode potential between -0.2 and 1.6 V (vs Ag/AgCl) in 0.5 M H₂SO₄ until the CVs characteristic for a clean electrode was obtained. Methanol electrooxidation measurements were carried out in a solution of 0.5 M H₂SO₄ containing 0.5 M methanol at a scan rate of 50 mV/s.

4.3. Characterization of Pt-Ru Nanospheres

Figure 4.1 shows TEM images of the obtained nanoporous Pt–Ru spheres synthesized under typical conditions (40 mol% Ru content in the precursor solution). The low magnification image (Please refer to Figure 4.1a) shows that each nanoparticle is assembled with many interconnected nanowires with a diameter below 3 nm to form a three-dimensional (3D) network of nanoarms with an outward open structure. The obtained spheres have well-defined dendritic nanoporous structures with randomly branched morphology and are remarkably uniform in shape without any formation of byproducts. The particle sizes were distributed in the range from 40 nm to 65 nm. To further characterize the Pt–Ru spheres, the edges of Pt–Ru branches were investigated by applying high-resolution TEM.
Figure 4.1. a) Low-magnification TEM image and and high-magnification TEM image of Pt–Ru spheres prepared from a typical solution (the Ru molar ratio in the precursor solution is 40%). b) High-magnification TEM image of the edge of a sphere. c) Selected area electron diffraction (ED) patterns taken from one sphere as shown panel a-2. d) High-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM) image and elemental mapping of Pt–Ru spheres prepared from a typical solution (Ru molar ratio in the precursor solution is 40%). Inset, elemental line scanning over the entire particle region highlighted.

As shown in Figure 4.1b, highly ordered lattice fringes with a d spacing of 0.225 nm corresponding to (111) planes of Pt–Ru face-centered cubic (FCC) structure were observed. Figure 4.1c shows the electron diffraction (ED) pattern of a selected area taken from a single Pt–Ru particle as shown in Figure 4.1a-2. As it can be seen from the pattern, two crystalline domains were oriented in a different way. Each particle did not show a single crystalline nature; instead, the atomic crystallinity coherently extended over several nanobranches to some extent. Next, the high-angle annular dark-field (HAADF) imaging technique was used to visualize the nanoporous structure in the Pt–Ru spheres. As indicated in Figure 4.1d, the
interconnected nanowires and empty spaces between the nanowires can be clearly distinguished due to differences in the contrast in the obtained image. The highly branched morphology of the spheres provides a high surface area. To determine the specific surface area, N\textsubscript{2} adsorption–desorption isotherms were recorded using the Brunauer, Emmett and Teller (BET) method. The specific surface area of the Pt–Ru spheres was 40 m\textsuperscript{2} g\textsuperscript{-1} (Please refer to Figure 4.2).

![N\textsubscript{2} adsorption isotherm for Pt-Ru spheres prepared from a typical solution (The Ru molar ratio in the precursor solution is 40 %).](image)

In this structure, guest species can easily gain access to the whole surface through the empty spaces between the Pt–Ru branches. Energy dispersive X-ray spectroscopy (EDS) analysis was also used to investigate the elemental distribution of Pt and Ru in an individual nanoparticle. As shown in Figure 4.1d, the line scans as well as elemental maps in a typical Pt–Ru sphere show a uniform distribution of Pt and Ru throughout the nanoparticle, thus providing evidence of the Pt–Ru alloy structure. The Ru content calculated by the elemental mapping was 8.9 atomic%, which was in good agreement with that obtained by inductively coupled plasma (ICP) analysis (9.2 atomic%).

Figure 4.3B shows the relationship between the Ru content in the resulting spheres and that in the used precursor solution. The obtained data were fitted to a third-degree polynomial function with a near perfect correlation (R\textsuperscript{2}=0.998).
Figure 4.3. A) Low-magnification TEM images of Pt spheres (a) and Pt–Ru spheres (b–f) prepared by using solutions with different compositions. The Ru/ Pt molar ratios in the used precursor solutions are (a) 0:100, (b) 5:95, (c) 10:90, (d) 20:80, (e) 40:60, and (f) 80:20. B) Relationship between the precursor compositions and the obtained product compositions. The product compositions were determined by ICP analysis.

Hence, the composition of Pt–Ru spheres could be easily and precisely tuned by changing the composition of the precursor solution. Also, it is worth to note that a similar behavior was observed for the synthesis of mesoporous Pt–Ru fibers using the lyotropic liquid crystal (LLC) method [34]. Noticeably, the Ru amounts in the deposited spheres were much lower than those in the used precursor solutions. For example, when the Ru concentration in the precursor solution was 40 atomic%, the Ru content of the deposited spheres was only 9 atomic%. In the present system, both Ru$^{3+}$ and [PtCl$_6$]$^{2-}$ ions are reduced in two steps, according to the following reactions [26, 36–38]:

\[
\begin{align*}
[\text{PtCl}_6]^{2-} + 2e^- & \rightarrow [\text{PtCl}_4]^{2-} + 2\text{Cl}^- & +0.68 \text{ V vs SHE} & \quad (4.1) \\
[\text{PtCl}_4]^{2-} + 2e^- & \rightarrow \text{Pt} + 4\text{Cl}^- & +0.76 \text{ V vs SHE} & \quad (4.2) \\
\text{Ru}^{3+} + e^- & \rightarrow \text{Ru}^{2+} & +0.25 \text{ V vs SHE} & \quad (4.3) \\
\text{Ru}^{2+} + 2e^- & \rightarrow \text{Ru} & +0.46 \text{ V vs SHE} & \quad (4.4)
\end{align*}
\]
According to the standard reduction potentials, Ru$^{3+}$ ions have a lower tendency toward reduction than [PtCl$_6$]$^{2-}$ ions. Therefore, the reduction of [PtCl$_6$]$^{2-}$ ions preferentially occurs, while Ru$^{3+}$ ions could not be simultaneously reduced with the same rate because of the slow rate of Ru reduction. To investigate the effect of the Ru content in the precursor solution on the morphology and composition of the final product, spheres were synthesized by using precursor solutions of various initial Ru content. As shown in Figure 4.3.A, all Pt and Pt–Ru spheres with various Ru contents possessed a dendritic structure. For all the samples, the BET surface areas measured by N$_2$ adsorption–desorption isotherms were over 40 m$^2$g$^{-1}$. These values are comparable or higher than those of most reported Pt-based catalysts. For example, the surface area of commercial Pt catalysts (Pt black, PB) ranges from 20 to 30 m$^2$g$^{-1}$. Dendritic Pt nanoparticles and Pt nanofoams have surface areas of 14 m$^2$g$^{-1}$ [6] and 27 m$^2$g$^{-1}$ [19], respectively. It is assumed that during the progress of the present synthesis, due to the effective interaction between the hydrophobic Poly (propylene oxide) (PPO) groups and the Pt surface, pluronic F127 chains were adsorbed on the surface of Pt, which can facilitate the growth of the dendritic structure [2, 3]. To further confirm the formation of alloy structure, the crystal structure of nanoporous Pt$_{91}$Ru$_{9}$ spheres synthesized under typical conditions was investigated by wide-angle XRD (Figure 4.4). The obtained XRD profile could be assigned to (111), (200), (220), (311), and (222) diffractions of a face-centered cubic (fcc) crystal structure. For comparison, the wide-angle XRD profile of nanoporous Pt spheres was obtained. It was observed that the XRD peaks for Pt–Ru spheres appeared at slightly larger angles than those for Pt spheres. To observe this shift in the peaks more clearly, very slow scanning was performed at the diffraction angle (20) from 80 to 82 degrees.
Figure 4.4. Wide-angle XRD patterns for (a) Pt spheres and (b) Pt-Ru spheres prepared from a typical solution (The Ru molar ratio in the precursor solution is 40 %:). Slow scanning XRD measurement (2θ = 80-82°) is shown as an inset image (The 311 peak position for the Pt sphere is noted by blue-colored line.).

As shown in the inset of Figure 4.4, the position of the (311) peak was slightly shifted to a larger angle for Pt–Ru spheres compared to that of Pt spheres. This peak shifting to larger angles indicates a decrease in the lattice constant, which confirms the successful incorporation of Ru atoms into the fcc crystal structure of Pt [23, 26, 33, 39-43]. Figure 4.5 shows the core level XPS spectra for the Pt 4f region of the resulting Pt–Ru alloy spheres (Pt91Ru9 and Pt95Ru5). The two peaks appearing at around 71.6 and 74.9 eV can be assigned to Pt 4f7/2 and Pt 4f5/2, respectively.
Figure 4.5. The core-level XPS spectra of the Pt 4f for the obtained Pt-Ru alloy spheres. The dotted colored line indicates the location of the Pt 4f$_{7/2}$ peak of pure bulk Pt.

As shown in Figure 4.5, the binding energy for the Pt$_{95}$Ru$_{5}$ alloy was clearly shifted to a higher value compared with the binding energy of Pt 4f$_{7/2}$ (71.39 eV [40], indicated by the dashed line) for the Pt spheres. With a further increase in the Ru content in the alloy, a slight shift to a higher binding energy was observed. Such a change in the electronic structure of Pt atoms by Ru incorporation is very common in alloy phase formation. This positive core-level shift can be attributed to an increase in the d vacancy [33] or downshift in the d-band center [32]. The modification of the electronic properties of Pt atoms improves the methanol oxidation reaction (MOR) activity by reducing the adsorption energy of CO on Pt which is formed during the methanol oxidation reaction [32–34]. To study the electronic structure of Ru, the Ru 3p region of the XPS spectra for Pt–Ru spheres was examined instead of the Ru 3d signal (main signal) because the Ru 3d region is always obscured by the C1s signal originating by carbon contamination of the surface. As shown in Figure 4.6, the XPS spectra of Pt–Ru alloys have two peaks centered at around 461 and 483 eV, which can be assigned to the Ru 3p$_{3/2}$ and Ru 3p$_{1/2}$, respectively. The Ru 3p$_{3/2}$ signal was deconvoluted into two peaks at 465.8 and 462.1 eV, which are attributed to Ru and RuO$_{2}$ respectively [41]. This shows that 92 atomic% of Ru in Pt$_{95}$Ru$_{5}$ and 90 atomic% of Ru in Pt$_{91}$Ru$_{9}$ were in their zero-valent metallic state.
As a preliminary demonstration, the electrocatalytic ability of the resulting Pt–Ru spheres with various compositions toward the methanol oxidation reaction was characterized by cyclic voltammetry in 0.5M H$_2$SO$_4$ electrolyte containing 0.5M methanol. For comparison, the electrocatalytic activity of Pt spheres and commercial Pt black powders was also measured and all the obtained current densities were normalized with respect to the loading sample amounts. As shown in Figure 4.7, the mass-normalized activity of Pt$_{91}$Ru$_{9}$ spheres was 206 mA mg$^{-1}$, a value around 2 and 4 times higher than those of Pt spheres and commercial Pt black, respectively. Generally, the ratio of the forward peak current density and reverse anodic peak currents ($I_f/I_b$) can be used to evaluate the tolerance of catalyst to carbonaceous species. Higher $I_f/I_b$ ratios indicate higher tolerance to CO poisoning [44, 45]. The $I_f/I_b$ ratio was 1.2 for Pt$_{91}$Ru$_{9}$ spheres, significantly higher than those for Pt spheres (0.95) and Pt black (0.98). This indicates an improvement in tolerance to CO poisoning due to the incorporation of Ru into the Pt catalyst.
Figure 4.7. Cyclic voltammograms (CVs) for methanol oxidation reaction and peak current densities for each sample. The currents are normalized by sample amounts. For comparison, commercially available Pt black powders are also measured.

### 4.4. Conclusion

Herein, I reported a facile, one-step, and low-cost method for the synthesis of nanoporous Pt–Ru spheres with high surface area using a commercially available block copolymer. The obtained spheres are composed of interconnected Pt–Ru nanowires that facilitate electron transport [35]. Such a unique dendritic nanoarchitecture, with an open nanoporous structure, is favorable for providing a high surface area and unblocked transportation of guest species such as methanol molecules.
4.5. References


Chapter 5

5. Rational Synthesis of Hollow Pt Spheres with Hollow Interior and Nanosponge Shell

5.1. Introduction

In the last decades, a great deal of attention has been paid to nano- and/or meso-structured materials with highly porous networks and high surface area due to their impressive industrial applications involving electrochemical catalysts, inclusion vessels, and adsorbents. Up to now, a wide range of compositions such as silica, carbon, inorganic–organic hybrids, polymers, and metals, have been successfully prepared by various methods [1, 2]. Recently, a great deal of effort has been devoted to the synthesis of metal-based nanostructures with high surface areas, because of their unique electrocatalytic properties [3]. In particular, Pt-based nanostructured materials have currently attracted widespread interest, because of their potential application as a catalyst in PEM fuel cells. Both soft- and hard-templates have been commonly employed for the synthesis of nanostructured Pt materials. In hard-templating method, well ordered mesoporous silica has been generally used as rigid templates [4–8]. Alternatively, soft-templates, such as surfactants, also can be used for the forming nanoporous structure [9, 10]. For instance, well-ordered mesoporous Pt can be easily prepared by chemical or electrochemical reduction of dissolved Pt salts in lyotropic liquid crystals made of highly concentrated surfactants [9–12].
To realize high Pt surface areas, there have been some reports on Pt hollow nanostructures, which have superior electrochemical properties [13–16]. So far, the Pt hollow nanostructures have been successfully synthesized by coating Pt on various spherical templates such as silica [13,17], Co [16,18], Ag [19–21] and other materials [14,22]. However, in all of these cases, complex procedures and the use of expensive materials as templates are employed, which is noneconomic for practical scale up. Furthermore, in the previous works, the Pt shell thicknesses were not precisely controlled [13–22]. The most disadvantageous point in the previous works is that the Pt shell of the hollow structures has no well-developed nanoporosity. Therefore, guest species from outside are not allowed to get access to inner parts of the hollow structures, resulting decreasing the effective Pt surfaces. Hence, the development of a facile and economic method for synthesis of Pt spheres with hollow interior and nanosponge shell with very high surface area is a practical and challenging issue to be solved urgently.

Herein, I proposed a facile and efficient method to prepare Pt spheres with hollow interior and nanosponge shell with high surface. Silica particles functionalized with amino group (with around 50 nm in diameter) were used as template to form the hollow interior, while nonionic surfactant assisted to create the Pt nanosponge shell [23,24].

**5.2. Experimental Section**

**5.2.1. Detailed Preparation Procedure**

For the preparation of the Pt hollow spheres, the surface of the silica particles was modified with aminopropyltriethoxysilane (APTES) firstly. The suspension of silica nanoparticles (Average particle diameter: 50 nm, Nissan Chemical Industries, Ltd.) was added to 50 ml tetrahydrofuran (THF) solution including 10 wt% APTES. After stirring for 12 h at room temperature, the APTES-modified silica particles were precipitated. Then, the modified silica particles were washed with THF and water in consecutive washing/centrifugation cycles for three times in order to remove excess APTES and form a smooth and homogenous layer of APTES on silica particles. In a typical synthesis, the organically modified silica particles (6.0 mg) was ultrasonically dispersed in 20 mM K₂PtCl₄ solution (7.5 ml) containing 0.05 g
Pluronic F127. Then, 0.1 M ascorbic acid (AA) (5 ml) was added, and the mixture was sonicated for 15 min. After washing three times with water, the product was added to 10 wt% hydrofluoric acid solution (20 ml) and placed for 3 days at room temperature in order to completely remove silica template. The final product was washed five times with water and dried at 45 °C.

5.2.2. Electrochemical Experiments

All cyclic voltammetry (CV) experiments were performed using a CHI 842B electrochemical analyzer (CHI Instruments, USA). A conventional three-electrode cell was used, including an Ag/AgCl (saturated KCl) electrode as a reference electrode, a platinum wire as a counter electrode, and a modified glassy carbon electrode (GCE) (3 mm in diameter) as a working electrode. The modified GCE was coated with the samples and dried at room temperature before each experiment. The loading amount in all of the samples was 3.0 μg. Methanol electro-oxidation measurements were performed in a solution of 0.5 M H2SO4 that contained 0.5 M methanol at a scan rate of 50 mV/s.

5.3. Characterization of Hollow Pt Nanospheres

Fig. 5.1 shows transmission electron microscopy (TEM) images of the hollow Pt spheres prepared under a typical solution with 7.5 ml Pt solution. The lower magnification image (Please refer to Figure 5.1a) revealed that the resulting Pt dendritic structure was assembled with plentiful interconnected nanowires with 2 nm in diameter. The Pt hollow particles were uniform in morphology without formation of by-products, demonstrating the high yield synthesis (Please refer to Figure 5.2a, b).
As shown in Figure 5.1b, lattice fringes with a d spacing of 0.23 nm were clearly observed, which corresponded to a \( \langle 111 \rangle \) plane of Pt face-centered cubic (FCC) structure.

In the present synthetic process, NH\(_2\)-modified silica particles were well dispersed in Pt precursor solution containing surfactants. Then, by addition of AA to the solution, the Pt deposition was occurred. At the early stages of the reaction, the Pt seeds were formed on the silica particle surface, because of the high surface affinity for the Pt seeds which is derived from the strong interaction between the amino group and the metal particles [25]. During the progress of the Pt deposition, the primary Pt seeds covering on the silica particles served as the nucleation sites for the further growth of Pt. At this stage, Pluronic F127 chains as a structure directing agent were absorbed on the surface of deposited Pt to facilitate the growth of the dendritic Pt shells [23, 24]. To elucidate the effect of amino modification on the silica surface, further investigation was performed in which silica particles without amino group were used as template (Please refer to Figure 5.2c). It was clearly revealed that the amino groups on the silica surface played a key role for making attachment sites for initial Pt seeds, whereas non-functionalized silica template could not act as template for the formation of hollow Pt spheres and led to the separation of silica particles and Pt dendrites (Please refer to Figure 5.2c)
Figure 5.2 (a) Low-magnification and (b) high-magnification SEM images of hollow Pt spheres (after silica removal) prepared using amino-functionalized silica particles under a typical solution containing 7.5 ml Pt solution. (c) Low-magnification SEM image of the deposited Pt obtained by using non-functionalized silica particles.

The SEM images clearly confirmed the three-dimensional (3D) globular shape and also clearly verified the empty spaces of highly branched nanowires (Please refer to Figure 5.2a and b). In the dendritic Pt shells, lots of Pt nanowires were highly branched and extended in various directions, to form an interconnected nanosponge structure. In such a nanoporous structure, accessibility to inner parts of Pt hollows is improved by the diffusion of guest species through empty spaces among interconnected nanowires. N₂ adsorption-desorption isotherm of the obtained Pt spheres gave a BET surface area of 36.3 m².g⁻¹ (Please refer to Figure 5.3), which is higher than the reported value (29.0 m².g⁻¹) for hollow Pt spheres prepared by photocatalytic reduction of Pt complex under light illumination [13]. For comparison, surface areas of commercial platinum catalysts (Pt black) ranges from 20 to
25m²·g⁻¹. The improved surface area was most likely derived from the presence of nanoporous dendritic shells.

![Image of N₂ adsorption-desorption isotherm of hollow Pt spheres](image)

**Figure 5.3.** N₂ adsorption-desorption isotherm of hollow Pt spheres prepared from a typical solution containing 7.5 ml Pt solution.

Furthermore, in this method, the Pt shell thicknesses could be precisely tuned by varying the amounts of Pt precursor. To investigate the effect of Pt amounts on the shell thicknesses, several hollow Pt spheres were synthesized with various amounts of Pt precursor solution in the range between 0.0 ml to 10 ml (The amounts of the added silica particles were fixed to 6.0 mg). TEM images of hollow Pt spheres after and before the silica removal were shown in Figure 5.4 and Figure 5.5, respectively. The average shell thicknesses were measured by TEM images (Please refer to Figure 5.6). The average shell thicknesses were proportionally increased with increasing the Pt amounts.
Figure 5.4. TEM images of hollow Pt spheres after silica removal. Various hollow Pt spheres were prepared from precursor solutions containing different Pt amounts. The amounts of added Pt solution are (a) 2.5 ml, (b) 5.0 ml, (c) 7.5 ml, and (d) 10 ml, respectively. The collapse of the hollow structures is indicated by black arrows, while the isolated Pt dendrite (as by-product) is indicated by white arrows.

It is noteworthy that in a small amount of Pt solution (2.5 ml), the hollow structures were mechanically unstable (Please refer to Figure 5.4a), because the spherical hollow nanostructures collapsed after the silica removal by HF treatment. When the amount of Pt solution was not enough, individual entities could not be joined well (Please refer to Figure 5.4b) and the hollow structures were destroyed easily. As shown in TEM images (Please refer to Figure 5.4a and b), the hollow structures prepared from 5.0 ml Pt solution collapsed partially.
Figure 5.5. TEM images of (a) the original silica template and (b–e) the obtained Pt products (before silica removal) prepared from precursor solutions containing different Pt amounts. The amounts of added Pt solution are (b) 2.5 ml, (c) 5.0 ml, (d) 7.5 ml, and (e) 10 ml, respectively.

In contrast, when the amounts of Pt solution were increased up to 10 ml, irregular Pt dendrites without inner hollows were formed as a by-product (Please refer to Figure 5.4d). The isolated Pt seeds nucleated, resulting in Pt dendrites independently grew. The optimum amount of Pt solution was found to be 7.5 ml. Under the optimized condition, after immobilization of Pt seeds on silica particles, Pt nanowires grew and branched out in various directions. Also, with the assistance of surfactants [23, 24], nanosponge shells consisting of interconnected highly branched nanowires were uniformly coated on the silica particle surface without by-products. Even after removing silica and applying the centrifugation and sonication processes, the hollow structures did not collapse, showing very mechanically stable robust hollows.
Figure 5.6. Relationship between the average Pt shell thicknesses and the added amounts of Pt solutions. The amounts of added Pt solution in the starting solutions are noted in parentheses.

As preliminary investigation on electrocatalytic activity of the obtained hollow Pt spheres with different shell thicknesses, methanol oxidation was measured by using cyclic voltammograms (CVs) method. Figure 5.7 shows mass-normalized activities. The Pt hollow particles with the lowest shell thicknesses (prepared with 2.5 ml Pt solution) exhibited the lowest catalytic activity. It can be supposed that access of methanol molecules to inner parts of catalyst was restricted, because Pt shells are collapsed and the Pt particles were highly aggregated (Please refer to Figure 5.4a).
Figure 5.7. Cyclic voltammograms displaying oxidation reaction of methanol, catalyzed by hollow Pt particles prepared from (a) 2.5 ml, (b) 5.0 ml, (c) 7.5 ml, (d) 10 ml Pt solution, respectively. For comparison, (e) commercially available Pt black powders are also measured.

With increasing the amounts of the Pt solution to 7.5 ml, electrocatalytic activity for methanol oxidation reaction was dramatically increased. The maximum electrocatalytic activity (80 mA.mg⁻¹) was around 1.7 times larger than that of commercially available Pt black. By improvement of mechanical stability of hollow structures, electroactive species could easily gain access to the whole surface of Pt through the hollow spaces. However, with the further increase of Pt amounts to 10 ml, the catalytic activity was decreased. As shown in TEM results (Please refer to Figure 5.4d), the formation of the undesired by-products and thicker shells prevented accessibility of methanol molecules to the whole exposed Pt surface. In other words, whole exposed Pt surface could not effectively act as reaction media.
5.4. Conclusion

I developed a facile method to synthesize hollow Pt spheres with tunable nanosponge shell thicknesses by using silica particles as templates. The obtained hollow particles possessed highly nanoporous structure, providing high surface area. Such a unique Pt nanostructure effectively improved the electrocatalytic performance as Pt catalysts by facilitating the access of electroactive species to the whole Pt surface. Currently, a great deal of attention has been attracted to the inorganic core-shell [26, 27] and hollow materials [28–34] in material research fields. However, their compositions have been very limited to polymers, silica, carbon, and metal oxides [26–34]. This synthetic concept can open a new avenue to create nanostructured metals.
5.5. References


Chapter 6

6. Design of Uniformly Sized Hollow Mesoporous Pt-Ru Particles

6.1. Introduction

Mesoporous materials have attracted much attention for years because of their beneficial uses as catalysts, catalysis supports, drug carriers, electric materials, and adsorbents [1-3]. Currently, hollow mesoporous materials are attracting fast-growing interests because of their low densities, high surface areas, high diffusion rates, and wide potential applications in various areas including catalysis, drug delivery, energy conversion, and storage system [4]. Many efforts have been made in the design and synthesis of hollow mesoporous materials with desired components. Several synthetic methods have been developed, including hard/soft-templating methods, selective etchings, Ostwald ripening or galvanic replacement processes, and Kirkendall effect-based methods [4-7]. Among these strategies, the hard-templating approach using silica spheres is an effective method for preparing hollow mesoporous silica and carbon particles with controllable cavity sizes. However, this method is ineffective for controlling the compositions of the synthesized hollow mesoporous particles, and the compositions have been limited to silica [5], carbon [6], and metal oxide [7]. Synthesis of metal particles consisting of mesoporous shells and hollow interiors remains a great challenge and will generate a new generation of electrocatalysts. Numerous research groups have studied the synthesis of mesoporous metals, owing to their high potentials in a
wide range of research fields [2b]. In particular, mesoporous Pt-based materials with high surface areas have recently attracted growing interest because they can be used as electrocatalysts [8]. Both hard-[9] and soft-[10] templating processes have been employed for synthesizing mesoporous metals. In spite of significant advances, however, the mesoporous metals produced by the previous methods have been limited to only simple architectures, such as continuous films and particles [9-10]. Hierarchical architectures of metals are considered to be essential for further upgrading their inherent functions. For example, as introduced above, the “hollow mesoporous structure” is expected to be a very promising architecture for improving electrocatalytic performance and utilization efficiency over its solid counterpart. In addition, through total control on characteristics of the hollow mesoporous structure (e.g., shell thickness, mesopore size, particle size, shape uniformity, and composition), we can exploit the full potential of mesoporous metals.

Our target in this study is synthesis of a new class of hollow mesoporous Pt-Ru and Pt particles with uniform sizes, named as “mesoporous metallic cells”. A dual-templating approach using colloidal silica particles and a non-ionic surfactant (Pluronic F127) has been demonstrated for the synthesis of the mesoporous metallic cells. In our strategy, the formation of mesoporous metal layer on the silica particles is conducted by utilizing a chemical reduction of metal species in the presence of low-concentrated surfactant solutions. The uniform mesopores in the shells as well as the large hollow interiors effectively facilitates diffusion of guest species from the outside. To achieve superior electrocatalytic performance, here I precisely controlled the shell thicknesses, compositions, and hollow cavity sizes, by changing the precursor solution amounts, precursor compositions, and silica particle sizes, respectively.

6.2. Synthesis of Mesoporous Pt and Pt-Ru Hollow Spheres

6.2.1. Materials

H₂PtCl₆, RuCl₃, and ascorbic acid (AA) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Pluronic F127 (Mw=12600) was obtained from Sigma. Commercial Pt black (HiSPEC® 1000) was supplied by Johnson Matthey Company.
6.2.2. Synthesis of Hollow Mesoporous Pt and Pt-Ru Particles

Firstly the surface of silica particles was functionalized with amine group. For this purpose, 50 mg of silica particles was well dispersed in the mixture of 10 ml of 2-propanol and 200 microlitre aminopropyltriethoxysilane (APTES) by ultrasonication. Then, the prepared suspension was kept at 80 °C for 12 hours. With the purpose of removing excess APTES and formation of a homogenous layer of APTES, the modified silica particles were collected and washed with ethanol and water in consecutive washing/centrifugation cycles for three times and then dried at room temperature.

In a typical synthesis of hollow mesoporous Pt-Ru particles, 4.2 ml of RuCl$_3$ solution (20 mM) containing 0.2M perchloric acid was mixed with 2.8 ml of H$_2$PtCl$_6$ solution (20 mM) (For synthesis of mesoporous Pt hollow particles, 7.0 ml of H$_2$PtCl$_6$ solution (20 mM) containing 0.2M perchloric acid was used.). Then, 2.0 mg of modified silica spheres was ultrasonically dispersed in the precursor solution. After dissolving Pluronic F127, 7.0 ml of 0.1 M ascorbic acid (AA) was added, and the mixture was sonicated in a water bath using an ultrasonic cleaner (US-2R, AS-ONE Co., Japan) for 4 h. The temperature of the sonication bath was kept constant at 35 °C by circulating water. After washing three times with water, the collected product was dispersed in 30 ml of 20 % hydrofluoric acid solution. The prepared suspension was shaken for 1 h and was left for 1 night at room temperature in order to completely remove silica template. Then, the hollow particles were washed five times with water and dried at room temperature for several days. For comparison, hollow mesoporous Pt particles were also prepared by using the precursor solution containing Pt and Pluronic F127. The removal of surfactants and silica spheres was confirmed by CHN and ICP analysis, respectively. The F127 with two PEO groups which can be dissolved in water was easily removed from the final product.

6.2.3. Electrochemical Measurements

The electrochemical properties were examined with a CHI 842B electrochemical workstation (CH Instrument Co., USA) utilizing a conventional three-electrode cell, including an Ag/AgCl electrode (as a reference electrode), a platinum wire (as a counter electrode), and a
modified glassy carbon electrode (GCE) with diameter of 3 mm (as a working electrode). The GCE was coated with the samples with the same metal loadings of 3.0 μg. Then 3.0 μl of 0.5 wt. % Nafion solution was dropped on the surface of the electrode. Finally, the as-prepared electrode was dried at room temperature. Prior to electrochemical experiments, the electrode was electrochemically cleaned by cycling the electrode potential between -0.2 and 1.6 V (vs Ag/AgCl) in 0.5 M H₂SO₄ until obtaining the typical characteristic CV for a clean electrode. Methanol electrooxidation measurements were performed in a solution of 0.5 M H₂SO₄ containing 0.5 M methanol at a scan rate of 50 mV·s⁻¹.

6.3. Characterization of Hollow Spheres

Figure 6.1 shows scanning electron microscopic (SEM) images of the obtained hollow mesoporous Pt-Ru particles with a uniform particle size of around 160 nm, synthesized under typical synthetic conditions. From high-resolution SEM images, well-defined mesoporous architecture was observed over the entire area of the external surface. The average shell thickness was around 28 nm. The mesopores were spherical shapes and remarkably uniform in size (The average pore size was around 8-9 nm). The corresponding N₂ sorption result gave a high BET surface area of 41 m²·g⁻¹. After addition of Ru to the precursor solution, the Ru content in the final product was increased up to 15 atomic%, as determined by inductively coupled plasma (ICP) analysis.
Figure 6.1. (a,c,d) SEM and (b) TEM images for hollow mesoporous Pt–Ru particles, named as mesoporous metallic cells, prepared under the typical conditions. (d) Enlarged image of the square area of (c).

As shown in Figure 6.2a-1, a bright center was surrounded by a dark peripheral area. Such a strong contrast clearly indicates the formation of a hollow interior structure. High-resolution TEM images clearly showed the lattice fringes with a \( d \) spacing of 0.225 nm, corresponding to the (111) planes of a face center cubic (fcc) crystal structure (Figure 6.2b) [11]. Selected-area electron diffraction (ED) patterns taken from one particle revealed the concentric rings attributed to (111), (200), (220) and (311) planes of a fcc crystal, indicating the polycrystalline nature (Figure 6.2b, inset). Line-scanning elemental mapping showed that both Pt and Ru were concentrated at the peripheral area according to the morphology of hollow particles (Figures 6.2c and d). The uniform distribution of both elements throughout the hollow particle also confirmed the formation of a Pt-Ru alloy structure.
Figure 6.2. (a-1) Bright-field and (a-2) dark-field TEM images for hollow mesoporous Pt–Ru particles prepared under the typical conditions. (b) Highly magnified TEM image of the edge part of hollow mesoporous Pt–Ru particles. Selected-area electron diffraction patterns taken from one particle is also shown as an inset image. (c) Elemental mapping of Pt and Ru. (d) Elemental distribution of Pt and Ru in the highlighted regions of (c).

To elucidate the formation of the Pt-Ru alloy structure, a typical sample was studied by wide-angle XRD and XPS measurements. As shown in Figures 6.3, the XRD patterns can be assigned to (111), (200), (220), (311), and (222) diffractions of a fcc crystal structure. Compared to hollow mesoporous Pt particles, the peaks for hollow mesoporous Pt-Ru particles appeared at slightly larger angles. To clearly illustrate this peak shifting, a XRD measurement was employed in the 2θ range of 79 to 85 degrees at a very slow scanning rate. As shown in the inset of Figure 6.3, the (311) peak shifted to a higher angle for hollow Pt-Ru particles than for hollow Pt particles, which is indicative of a decrease in the lattice constant and verifies a successful incorporation of Ru atoms into the Pt crystal lattice.
Figure 6.3. Wide-angle XRD patterns of hollow mesoporous Pt-Ru and Pt particles. Slow scanning XRD profile at $\theta = 79\text{-}85^\circ$ is also shown as an inset image. The blue-colored line indicate the (311) peak position for mesoporous Pt hollow particles.

Figure 6.4 shows the XPS spectra for the Pt 4f region for hollow Pt-Ru and Pt particles. Two peaks appeared in the XPS spectra at around 71.3 and 74.6 eV, corresponding to Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$, respectively. The binding energy (BE) of Pt 4f$_{7/2}$ for hollow Pt-Ru particles was clearly shifted to a higher BE than for hollow Pt particles. Such a significant change in the electronic state of Pt atoms caused by Ru incorporation confirms the formation of an alloy phase.
In the present synthetic strategy, amino-modified silica particles are completely dispersed in a precursor solution containing metal ions (Pt and Ru species) and F127 surfactant. The aggregation behavior (i.e., unimer-to-micelle transition) of F127 molecules is strongly affected by temperature. It has been reported that with a change of temperature from 10 °C to 30 °C, the corresponding critical micelle concentration (CMC) of F127 decreases from 1.75 wt% to 0.008 wt%. Because our synthetic temperature was set at exactly 35 °C, the F127 concentration in this study (around 0.5 wt%) was surely above the CMC, and the dissolved F127 molecules were thought to form spherical micelles. Owing to an effective interaction between coordinated waters of metal-aqua complexes and ethylene oxide groups, sufficient metal species are expected to cover the micelle surface [13].

To further investigate the formation mechanism, the shell structures were investigated in a time-dependent TEM observation (Figure 6.5). After addition of ascorbic acid, the reduction of Pt and Ru species occurred only on the silica surface (Figure 6.5a). Due to high affinity between amino groups grafted on the silica surface and metal seeds, initially deposited Pt-Ru seeds favored covering the silica particles. Recent studies have reported new insight into the self-assembly of surfactants and discussed the formation of their adsorption layer on the
liquid-solid interfaces [14]. Such adsorption process can be further accelerated by forming hydrogen bonds between terminal hydroxyl groups in the F127 surfactant and amino groups on the silica particles.

![TEM images of Pt-Ru samples (before silica removal) taken at different reaction times](image)

Figure 6.5. TEM images of Pt-Ru samples (before silica removal) taken at different reaction times ((a) 0.5 h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h, and (f) 6 h).

This interaction leads to efficient organization of surfactant molecules into an ordered array at solid-liquid interfaces [15]. In our case, coupling the surface assembly of surfactant micelles with chemical reduction of the metal species is the key point in generating mesoporous structures [13], which is in complete contrast to conventional synthetic methods such as hard- and soft-templating methods [9-10]. The initial metal seeds can act as nucleation sites for further growth of the Pt-Ru alloy (Figure 6.5a and b). With increasing reduction time, well-defined mesoporous structures could be gradually developed, resulting in robust hollow mesoporous particles (Figure 6.5 c-f). The hollow cavity was easily and precisely tuned by
using colloidal silica particles with different sizes. Figures 6.6 shows SEM and TEM images of hollow mesoporous Pt-Ru particles in which silica spheres with an average size of 520 nm were used.

![SEM and TEM images of hollow mesoporous Pt-Ru particles](image)

Figure 6.6. (a, c) SEM and (b, d) TEM images for hollow mesoporous Pt-Ru particles with large hollow cavity.

Thus, a large hollow space reflecting the size of the initial silica particles were obtained successfully. Furthermore, the shell thicknesses could be controlled by changing the amounts of metal species dissolved in the precursor solutions. Several hollow mesoporous Pt-Ru particles were synthesized with different amounts of metal salts, i.e., the added amounts were changed from 3.5 ml to 7.0 ml and 10.5 ml, while the amount of colloidal silica particles and Pt/Ru molar ratio were fixed at 2 mg and 40/60, respectively. As shown in Figures 6.7 a-c, the
average shell thicknesses measured from TEM images increased proportionally to 13, 28, and up to 42 nm, respectively, as the amounts of the dissolved metal species were increased.

Figure 6.7. (a-c) TEM images for hollow mesoporous Pt-Ru particles with different shell thicknesses. (d) SAXS profiles for mesoporous Pt-Ru hollow particles with different shell thicknesses

The SAXS measurement confirmed the structural features observed by TEM. Figure 6.7d shows the SAXS curve of hollow mesoporous Pt-Ru particles with different shell thicknesses, where $q$ is the magnitude of the scattering vector. As highlighted by blue region in Figure 6.7d, the very broad peak at $q \sim 0.5 \text{ nm}^{-1} (d = 12.5 \text{ nm})$ is ascribed to the average distance between the mesopores as observed by SEM (Figure 6.1). With the increase of shell thicknesses, the peaks became more intense, in which the number of mesopores was increased (Figure 6.7 a-c). The peaks indicated by red-colored lines can be attributed to the appearance of the spherical cores of the hollow particles. Because the particles are aggregated, it is reasonable to suppose that the system consists of the spherical particles embedded in a metal medium, rather than a well-dispersed core-shell particle system. The theoretical form factor
\( P(q) \) for spherical pores with the radius \( R \) is expressed as \( P(q) = \frac{3(\sin qR - qR \cdot \cos qR)}{(qR)^3} \).

The theoretical curve for \( R = 37 \) nm, which corresponds to the radius of hollow size of the particles as observed by TEM (Figure 6.7 a-c). The positions of the peaks in the theoretical curve are mostly in accordance with those in the experimental curves.

### 6.4. Effect of Acidity and Surfactant Concentration on Final Products

The reducing capacity of AA could be modulated by adjusting the pH value of the aqueous solution. When HCl added to precursor solution, the reduction rate of Pt ions is dramatically decreased compare to precursor solution without acid. These observations are consistent with the decrease of reducing capacity of AA with decreasing pH. As shown in Figure 6.8, at higher HCl content (low pH), the morphology of obtained Pt shell also changed from dendritic to mesoporous structure. In our proposed method, because of the interaction between PEO groups of F127 and amino groups, surfactant micelles are adsorbed on the amino modified silica spheres and act as template to create mesoporous structure. This mechanism is completely different from the formation of dendritic Pt shell on silica under the fast growth conditions, as precursor reduction with AA is more facile at high pH.

![SEM images](image)

Figure 6.8. SEM images for hollow mesoporous Pt particles by using a precursor solution (a) without acid and (b) with 65mM HCl (pH=0.76)
To study the effect of surfactant concentration, I also changed the concentration of surfactant in the precursor solution. When the F127 concentration decreased from 0.5 wt% to 0.03 wt%, the mesoporous structure on the surface completely disappeared (Figure 6.9). Thus, the use of F127 is vital for the formation of mesopores and it is proved the F127 micelles can serve as the structure-directing agent effectively.

Figure 6.9. SEM image of the deposited Pt samples obtained by using a precursor solution (a) without F127, with (b) 0.03 wt% and (c) 0.5 wt% F127.

6.5. Electrocatalytic Activity toward Methanol Oxidation Reaction

As a preliminary demonstration of electrocatalytic activity of the prepared samples toward the methanol oxidation reaction (MOR), the electrocatalytic activity of several samples with different shell thicknesses was examined using a cyclic voltammetry method in 0.5 M H₂SO₄+0.5 M methanol electrolyte (Figure 6.10). For comparison, electrocatalytic activity of commercial Pt black was measured as well. All the obtained currents were normalized with respect to the loaded amount of sample. As shown in Figure 6.10b, hollow mesoporous Pt-Ru particles with a thin shell (around 13 nm) showed the highest current density (384 mA·mg⁻¹). This value was much higher than those of other samples, such as hollow mesoporous Pt (89 mA·mg⁻¹), commercial Pt black (82 mA·mg⁻¹), and commercial activated carbon with Pt nanoparticles (136 mA·mg⁻¹), and also around twice higher than those of dendritic Pt-Ru spheres with almost the same Pt-Ru composition [16].
Figure 6.10. Demonstration of methanol oxidation activity. (a) Cyclic voltammograms for hollow mesoporous Pt-Ru particles with different shell thicknesses and commercial Pt black. The obtained currents are normalized by the sample amounts. (b) Summary on the mass-normalized activities and the CO tolerance for all the samples. As references, hollow mesoporous Pt particles and commercial Pt black are compared.

As seen in Figure 6.10b, however, with the increase of the shell thicknesses in hollow mesoporous Pt-Ru particles, the current densities were gradually decreased. The efficiency of an electrocatalytic reaction is strongly dependent on the accessibility of the reactants to the catalysts [17]. In the case of hollow particles with large shell thicknesses, the methanol electrolyte cannot gain access to inner parts of the thick shell. In other words, all of the metal surface cannot work well as an electroactive surface. Precise control of the shell thickness is necessary for the enhancement of the catalytic activity. 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.
6.6. References


Chapter 7

7. Synthesis and Characterization of Pd@Pt Concave Nanoparticles

7.1. Introduction

Recently, much attention has been paid to the synthesis of metal concave nanoparticles because of their potential use as catalysts in a wide range of reactions with different industrial and technological applications. Concave nanoparticles with high indexed facets and high density of valency unsaturated atoms in edge and kinks showed unusual physiochemical properties and demonstrated high catalytic activity, especially in electro-oxidation reactions [1-3]. In particular, bimetallic concave nanoparticles have recently attracted growing interest because of their superior catalytic activities over their monometallic counterparts. The enhanced properties can be attributed to the synergetic effect of second metal [3, 4].

The synthesis of concave nanoparticles is not facile and straightforward, because the formation of concave morphology is not favored by thermodynamics. Even though novel synthetic methods using preformed metal seeds, precise kinetic control and various chemical additives could address these thermodynamic limitations, in all of these approaches, complicated procedures including at least two steps and/or high pressure and temperature conditions are required [5-7].

In spite of the recent significant advancements in the synthesis of concave nanoparticles, facile and one step synthesis of bimetallic concave nanoparticles is still challenging issue to be solved. In addition, the fabrication of metal concave nanoparticles with deep concavity to provide high surface to volume ratio is another challenging issue in this field. To overcome these limitations of previous approaches, a template method is introduced for one-pot and facile synthesis of concave nanoparticles. The advantage of the template method for the fabrication of concave nanoparticles is that the morphology of the product is mainly determined by the shape of the template and hence these methods are less sensitive to synthesis conditions. In our proposed method, surfactant micelles which are formed on the primary metal seeds act as growth barrier to create concave structure. To fully demonstrate this new approach and its application for the synthesis of hierarchical and multifunctional concave nanostructures, I successfully synthesized Pd@Pt nanoparticles with deep concavity and dendritic structure. It should be noted that, in the case of heterogonous bimetallic structures, the synthetic conditions are more complicated relative to monometallic particles owing to difference in reduction rate of metal salts and the different tendency of structural directing agents for interaction with metal surfaces.

The essence of our proposed method is to take the advantage of self assembly of surfactants into hemimicelles and their function as template for the synthesis of concave nanoparticles. Previous studies on the interaction between surfactant and solid substrate at the solid-water interface provide insight into the tendency of surfactant molecules to be adsorbed on the solid surface and self assemble into micelles or hemi-micelles on the liquid-solid interfaces [8-11]. In the case of nonionic molecules of surfactant, they are mainly adsorbed physically on the hydrophobic adsorbent and if the concentration is over CMC, they form hemimicelles to be stable thermodynamically [12]. Such an interesting phenomenon offers the groundwork for the rational design of novel concave nanoparticles. Coupling the self assembly of hemimicells on metal seeds with the coalescence of tiny metal seeds and formation of highly branched structure enables us to synthesize complex concave metal nanoparticles with nanoporous structure which cannot be achieved with conventional synthetic methods such as seeded growth and site-specific etching.
7.2. Synthesis of Pd@Pt Nanoparticles

To create concave metal nanoparticles with nanoporous structure, 20 mg of Pluronic F127 were ultrasonically dissolved in the precursor solution containing 1.2 ml of K$_2$PtCl$_4$ (20 mM) and 0.8 ml of PdCl$_2$ (20 mM) solution and hydrochloric acid (65 mM). After adding ascorbic acid as a reducing agent, the mixture was continuously sonicated in a water bath for 2 h.

7.3. Characterization of Pd@Pt Nanoparticles

Figure 7.1 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the concave Pd@Pt nanoparticles synthesized under the typical conditions. As shown in Figure 7.1 c and d, every dendritic Pd@Pt nanoparticles contains several well defined and deep concavities.

Figure 7.1. (a, c, d) SEM and (b) TEM images of dendritic Pd@Pt concave nanoparticles
For further investigation of nanoparticles, high resolution transmission electron microscopy (HRTEM) was applied to characterize the nanostructure of an individual particle (Figure 7.2a). Pores and their walls can be clearly distinguished because of differences in the contrast in HRTEM image. The well developed branched structure of the walls can also be observed in both Figures 7.2a and 7.2b).

![HRTEM images of Pd@Pt nanoparticles](image)

Figure 7.2. (a) Bright-field and (b) dark-field TEM images for Pd@Pt nanoparticles prepared under the typical conditions. (c) Elemental mapping of Pd@Pt. (d) Elemental distribution of Pt and Pd in the highlighted regions of (b).

As shown in Figure 7.2c and 7.2d, the elemental maps as well as line scans clearly showed that Pd was concentrated in center, whereas Pt was concentrated at the outer edge of the nanoparticle. From these energy dispersive X-ray spectroscopy (EDS) data, it was revealed that Pt and Pd were distributed according to the morphology of the Pd@Pt core-shell nanosphere. This elemental distribution of Pd and Pt is a direct evidence of the formation of a Pd@Pt core–shell structure. The Wide angle X-ray diffraction (XRD) Pattern of Pd@Pt
nanoparticles showed a face-centered cubic (FCC) crystal structure (Please refer to Figure 7.3).

![Wide-angle XRD patterns of Pd@Pt nanoparticles.](image)

Figure 7.3. Wide-angle XRD patterns of Pd@Pt nanoparticles.

Low-magnification TEM and SEM images (Please refer to Figure 7.4a – 7.4d) clearly shows that nanocolloids are remarkably uniform in size and morphology without any formation of by-products, demonstrating the high yield (∼100%) synthesis of the Pd@Pt nanoparticles. The size distribution of the nanocolloids was 38-49 nm, with an average size of 44 nm.
Figure 7.4. Low magnification (a, c, d) TEM and (b) SEM images of dendritic Pt@Pd concave nanoparticles

N$_2$ adsorption-desorption isotherm of the resulting Pseudo Pd@Pt nanospheres gave a large BET surface area of 40 m$^2$/g (Please refer to Figure 7.5). In the present study, F127 hemimicelles directly act as a template and structural directing agent to form well defined concave morphology with an open structure. The Pd content in the nanoparticles determined by inductively coupled plasma (ICP) analysis was 15 at.%.
To further elucidate the formation mechanism of Pd@Pt nanoparticles, the synthesis progress was studied stage by stage using TEM images. Obtained images provide insight into the formation mechanism of nanoparticles. In the present system, according to the standard reduction potentials, Pd$^{2+}$ ions have a higher tendency toward reduction than [PtCl$_4$]$^{2-}$ ions (Pd$^{2+}$/Pd: +0.915 V vs SHE and [PtCl$_4$]$^{2-}$/Pt: +0.755 V vs SHE). Therefore, the reduction of Pd complexes preferentially occurs in a short time to form initial metal seeds (Please refer to Figure 7.6a). Due to the interaction between the hydrophobic PPO groups and the metal surface, the F127 molecules adsorbed on the primary metal seeds and form hemimicelles on the seed-solution interface. These hemimicelles act as template for the further deposition of Pd and subsequent overgrowth of Pt on Pd seeds resulting in the formation of concave morphology (Please refer to Figure 7.6 b- 7.6 d). After a period of 2 hrs, the Pt shell growth was terminated and the size and morphology of nanoparticles were not changed anymore (Please refer to Figure 7.6d and 7.6e).
In this approach, the Pd core size was easily tuned by changing the molar ratio of Pt/Pd in the precursor solution. Figure 7.7 shows TEM images of Pd@Pt nanoparticles in which the molar ratio of Pt/Pd was changed from 9 (typical sample) to 4. As shown by elemental analysis, the Pd core size is around 47 nm which is around 1.8 times larger than that of the typical sample.
Figure 7.7. (a) Bright-field and (b) dark-field TEM images for Pd@Pt nanoparticles. (c) Elemental mapping of Pd@Pt. (d) Elemental distribution of Pt and Pd in the highlighted regions of (b). The Pt/Pd molar ratio used in the starting solution is 4.0

7.4. Conclusion

The synthesis of Pd@Pt nanocolloids with concave Surfaces is reported by one-step and efficient wet-chemical route. The key important factors in the proposed method are self assembly of surfactant micelles in the low concentration surfactant solutions and precise control on the reduction rate by adding acid to the precursor solution. 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. During the reduction of metal ions, F127 micelles act as template to form mesoporous Pd@Pt nanoparticles.
7.5. References


Chapter 8

8. General Conclusions and Future Prospects

8.1. General Conclusions

Synthesis of nanoporous metal particles with desired shape and morphology has attracted a great deal of attention, because of their widespread use in energy conversion/storage devices, sensors, and catalysts. In spite of the recent significant advancements in synthesizing porous nanoparticles, 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. In addition, most of these methods have poor yield of a given morphology. In the case of mesoporous particles, synthetic approaches are mainly limited to producing simple structures such as nanoporous large particles with irregular morphologies (Please refer to Table 8.1). To address these challenging issues, I was motivated to design a general straightforward approach for the high yield synthesis of nanoporous particles with uniform size and morphology. Because of the simplicity and scale-up ability of solution-phase methods, I adopted a solution-phase strategy for the synthesis of nanoporous metal particles with diverse shape and morphologies.
Table 8.1. A few examples of nanoporous metal particles prepared by previous methods.

<table>
<thead>
<tr>
<th>Product</th>
<th>Method</th>
<th>Shape</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–Pd alloy nanocages</td>
<td>Galvanic replacement method</td>
<td>a)</td>
<td>[1]</td>
</tr>
<tr>
<td>Pd@Pt core-shell nanoparticle</td>
<td>Seeded growth method</td>
<td>c)</td>
<td>[2]</td>
</tr>
<tr>
<td>Dendritic Pd nanoparticles</td>
<td>Crystallite coalescence</td>
<td>b)</td>
<td>[3]</td>
</tr>
<tr>
<td>Mesoporous Pt particles</td>
<td>Hard template (KIT-6)</td>
<td>b)</td>
<td>[4]</td>
</tr>
<tr>
<td>Mesoporous Pt–Au Binary Alloys</td>
<td>Soft template (LLCs)</td>
<td></td>
<td>[5]</td>
</tr>
</tbody>
</table>
As shown in Figure 8.1, all the nanoporous structures were simply synthesized by purposefully changing the synthetic parameters including precursor composition (e.g. type and concentration of metal salts and surfactants, and pH) and synthetic conditions (e.g. synthetic temperature and ultrasonic irradiation).

**Proposed Solution Phase Synthesis Framework**

*Precursor composition*
- Metal Salts (type, concentration)
- Surfactants (type, concentration)
- Acidity (pH)

*Synthesis Conditions*
- Temperature
- Ultrasonic Irradiation

*Different Compositions*
- Single
- Binary

*Different Structure*
- Core-Shell
- Dendritic
- Hollow
- Mesoporous

Figure 8.1. Proposed solution phase synthesis framework

The effect of the synthetic conditions on the final morphology of products was carefully discussed. The formation of different structures and the quality of product were correlated with the nucleation and growth conditions. The correlations are explained in terms of surfactant micellization and reduction kinetics. I also demonstrated that a broad range of hierarchical nanostructures can be synthesized through a proper control on the synthetic parameters (Please refer to Figure 8.2). In this chapter, general conclusions and prospective directions of my research are presented.
8.1.1. Synthesis and Characterization of Dendritic Metal Particles

In Chapters 2-5, a direct chemical approach for the synthesis of dendritic nanoporous metals with different structures and compositions was presented. In Chapter 2, I reported the template-less synthesis of nanoporous Au sponge by a rapid and one-step method at room temperature. In this route, precursor solution containing Au salt was simply mixed with sodium borohydride (SBH) solution. Since the reduction force of SBH is very strong, the SBH molecules release numerous electrons by self-decomposition in the aqueous solutions. Therefore, a large amount of hydrogen bubbles is generated during the Au deposition, forming the voids with different sizes in the products. Although resulting particles showed porous structure but there is no control on particle size and size distribution. To further control the particle size, ascorbic acid as a mild reducing agent is replaced with SBH and F127 added to the precursor solution as stabilizer. Even though resulting Au nanospheres did
not show any porosity, they are used as nucleation site for the overgrowth of nanoporous Pt.
For this purpose Pt salt is also added to the initial precursor solution to obtain dendritic Au@Pt nanoparticles (Please refer to Chapter 3). Because of the different reduction potentials of the two soluble metal salts (Au (III) and Pt (IV) 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 structure on the Au seeds, which is confirmed by ultraviolet-visible light absorption spectroscopy and transmission electron microscopy. X-Ray elemental mapping and X-ray diffraction (XRD) patterns confirmed the formation of core-shell structure. When mixing of the precursor solution with a magnetic stirrer was replaced with the ultrasonic treatment, the particle size was dramatically decreased and their size distribution became very narrow. It could be attributed to the change of nucleation mechanism from a progressive regime to an instantaneous one due to acoustic cavitation. Thanks to effective increase of electrochemically active surface area and electronic modification of Pt atoms by Au core, the Au@Pt nanocolloids realized 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. This is truly the first report on the one-step synthesis of core-shell nanospheres.

If the difference in the reduction rate of two metal salts in precursor solution is less, instead of the core-shell structure, alloy particles can be formed. Alloying the oxophilic metals (e.g., Ru, Pd, and Ni) to Pt plays a key role in reducing CO poisoning and improving the catalytic activity. Among all of these alloys, Pt-Ru catalyst is the most advantageous catalyst for catalytic reactions and shows enhanced CO tolerance in methanol oxidation reaction. As mentioned in chapter 4, the co-reduction of Pt and Ru salts lead to the synthesis of Pt-Ru nanoparticles with dendritic structure. The obtained spheres with well-defined dendritic structure are characterized by TEM, XRD and XPS. Electrochemical experiments showed high catalytic activity toward methanol oxidation reaction as well as drastic improvement in tolerance to CO poisoning. This improvement is caused by the bi-functional effect of Ru and electronic modification of Pt atoms. Thus, this one-step approach with low-concentration surfactant solution is widely applicable to other metal, alloy and core-shell systems.
By coupling hard templates with this method, more complicated structures like dendritic hollow nanoparticles can be achieved. Chapter 5 describes the synthesis of hollow Pt spheres with dendritic shell by using amino-modified silica particles as template. Because of the strong affinity between tiny metal seeds and amino-modified silica spheres, Pt seeds were adsorbed on the silica surface and self-assembled to form the dendritic Pt shell. Interestingly, the Pt shell thickness was simply tuned by varying the amounts of Pt precursor. Such a unique Pt nanostructure with hollow interiors effectively improved the electrocatalytic performance as a Pt catalyst by providing high surface area.

8.1.2. Synthesis and Characterization of Mesoporous Metal Particles with Well-Defined Hierarchical Porosity

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, I further optimize the above general synthesis framework described in Chapters 2-5 in order to achieve mesoporous structures with well-defined hierarchical porosity for high catalytic performance. In such a unique structure, dendritic structure contributes to high surface area with a great deal of active sites for catalytic reactions and mesopores can facilitate mass transport in nanoporous catalyst. In Chapters 6 and 7, new approach for the synthesis of mesoporous materials with uniform pore sizes is proposed and developed. In this approach, coupling the self assembly of micells or hemimicells on solid-liquid interface with coalescence of tiny metal seeds and formation of dendritic structure enables us to synthesize complicated mesoporous architectures with multifunctional properties which cannot be achieved using conventional synthetic methods of mesoporous metals (i.e., hard- and soft-templating approaches).

In Chapter 6, a new class of hollow mesoporous Pt and Pt-Ru particles with a uniform size, named as “mesoporous metallic cells”, is presented. For the synthesis of mesoporous Pt hollow spheres, the mentioned synthetic conditions in chapter 5 (synthesis of dendritic hollow Pt spheres) are modified by decrease of pH to modulate the reduction rate of Pt ions and increasing the synthetic temperature to stabilize the F127 micelles. Mesoporous metallic cells
are prepared by a dual-templating approach using colloidal silica particles and non-ionic surfactant micelles. The reducing capacity of ascorbic acid is modulated by adjusting the pH value of the aqueous solution. When HCl added to precursor solution, the reduction rate of Pt ions is dramatically decreased compared to the precursor solution without acid. These observations are consistent with the decrease of reducing capabilities of ascorbic acid with decreasing pH. At higher HCl content (low pH), the obtained Pt shells exhibited mesoporous structures. In this proposed method, because of the interaction between PEO groups of F127 and amino groups of silica, surfactant micelles are adsorbed on the amino modified silica spheres and act as template to create mesoporous structure. This mechanism is completely different from the formation of dendritic Pt shell on silica under the fast growth conditions, as precursor reduction with ascorbic acid is more facile at high pH. As control experiments, I also changed the concentration of surfactant in the precursor solution. When the F127 concentration decreased from 0.5 wt% to 0.03 wt%, the mesoporous structure on the surface completely disappeared. To realize the full potential of mesoporous metals as electrocatalysts, mesoporous Pt-Ru hollow spheres was prepared by adding RuCl₂ to the precursor solution. I also precisely control the shell thickness, composition, and hollow cavity size by changing the precursor amount, precursor composition, and silica particle size, 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. Due to synergetic effect of Ru, typical sample showed enhanced CO poisoning and electrocatalytic activity toward methanol oxidation reaction.

This synthetic concept is extended to the synthesis of interesting nanospheres with uniform mesopores on surface. In Chapter 7, I demonstrated that the use of surfactant assembly in aqueous solution phases can lead to formation of mesoporous Pd@Pt core-shell nanoparticles. In this proposed method, 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. During the reduction of metal ions, F127 hemi-micelles which were formed on the primary metal seeds act as growth barrier to create concave surface. I believe this method can be extended to fabrication of many other metals and their alloys by designing appropriate precursor solutions.
8.2. Future Prospects

In the recent years, porous metals have attracted a great deal of attention because of their catalytic applications in electrochemical reactions in fuel cells. In spite of the recent significant advancement in porous catalysts, there are some challenges for the widespread use of Pt-based catalysts such as short life-time and CO poisoning. Because the catalytic properties of catalysts are highly depended on their structure and composition, catalytic properties of Pt catalysts can be improved by further modification of the composition and morphology of catalysts. As a future plan, I am going to study “the synthesis of multi-layer hollow particles” and “development of nanoporous metals with hierarchical porosity”.

8.2.1. Synthesis of Multi-layer Hollow Particles

Recent studies show that novel interesting Pt-based structures such as hollow structures have superior properties such as low density and high specific surface area to offer high electrocatalytic performance and utilization efficiency. On the other hand, considerable improvement was observed in catalytic properties of Pt catalysts by adding a supporting layer of other oxophilic elements (e.g., Ru, Pd, and Ni). Hence, nanoporous multi-layer hollow particles composed of Pt, Ru and Pd layers with fully developed nanoporosity can provide high surface area and high catalytic activity. In addition, because of the accessibility of reactant to the bimetallic heterointerfaces (i.e. Pt-Ru and Pt-Pd), it can show enhanced CO poisoning. Such a unique structure can be prepared using layer by layer deposition of Pd, Pt and Ru on the silica particles and then removing silica by treating with HF. Because of the simplicity and flexibility of the proposed solution phase method in this thesis, it can be adopted for depositing metal layers.

8.2.2. Development of Nanoporous Metals with Hierarchical Porosity

Although different mesoporous structures with high surface area and open structure have been successfully achieved, none of them shows the hierarchical porosity in the nanoporous framework. In nanoporous metals with hierarchical porosity, large pores contribute to facilitate the transportation of reactants and products in porous catalysts and smaller pores
(meso-or nano pores) provide high active surface area. Hence, in heterogeneous catalytic reactions, hierarchical porosity can effectively improve the diffusion rate and increase the catalytic performance. Using suitable hard template associated with self-assembled micelles can be a good method to fabricate such a hierarchical porosity.
8.3. References


List of Achievements

Papers


Presentations

1. Block Copolymer Assisted Synthesis of Microspheres with Au@Pt Core and Dendritic Pt Shell (Poster Presentation), The 4th Global COE International Symposium on ‘Practical Chemical Wisdom’, Tokyo, Japan. (January 14, 2010), H. Ataee-Esfahani, L. Wang, Y. Yamauchi

2. Synthesis of Dendritic Au@Pt Core-Shell Nanoparticles (Poster Presentation), JSPS A3 Foresight Seminar: Present Status and Future Prospects of Mesoporous Materials, Tokyo, Japan (September 3, 2010), H. Ataee-Esfahani, L. Wang, Y. Yamauchi

3. Facile Synthesis of Nanostructured Pt Hollow Spheres with High Surface Area (Poster Presentation), The 2nd NIMS-Waseda International Symposium, Tsukuba, Japan (December 1, 2010), H. Ataee-Esfahani, Y. Yamauchi


5. Synthesis of Nanostructured Pt-Ru Particles toward Highly Active Electrocatalysts (Poster Presentation), Third NIMS-Waseda International Symposium, Tokyo, Japan (November 1, 2011), H. Ataee-Esfahani, Y. Yamauchi
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