

Synthesis of Rh-Pd-Pt Alloy Nanoparticles by Femtosecond Laser Pulse Irradiation

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論文内容要旨

Nanoscience and nanotechnology have attracted a great deal of interest for scientists and engineers in almost all disciplines. Understanding of the properties of metal and alloy nanoparticles (NPs) and exploring their potential application is a major driving force behind the synthesis of a large variety of nanomaterials. This is due to the fact that a number of physical and chemical properties including optical and magnetic properties, specific heats, melting points, and surface reactivities are strongly size-dependent. There are two routes to synthesize metal NPs, namely, top-down and bottom-up approaches. Conventional top-down approach is being replaced by bottom-up approach to date. This strategic replacement would synchronize in the existing areas of nanoscience such as opto-electronics, catalyst, sensing and medicine. The size, shape and composition of metal and alloy NPs can be controlled much more easily by bottom-up approach. Generally, the end products of bottom-up method are referred to “colloidal NPs”, as the particles are formed in the presence of liquid solvent where the ions mixed with some additives to keep the NPs stable for longer period of time. Once colloidal metal and alloy NPs can be fabricated precisely in size, shape and composition, they may reveal many interesting physical and chemical properties that could be ideal as building blocks for engineering and tailoring nanoscale structures for specific technological applications.

To synthesize colloidal metal NPs using bottom-up method, reduction of ions in the solution is standard. Depending on the situation, the reduction of ions is performed not only by the addition of reducing agent in chemical method but also by applying an energetic field such as ultrasonic and electromagnetic waves. To produce metal NPs, different approach has been briefly reviewed. Every method possesses both advantages and disadvantages. There is an increasing demand to develop high yield, low cost, non-toxic and environmentally friendly procedure to synthesis metal or alloy NPs. Synthesis of metal or alloy NPs using femtosecond laser would be expected to become an entirely new type of process due to the characters like highly spatial resolution, reaction selectivity, reaction controllability, and shape conversion via photo-irradiation. According to the flexibility of laser to focus in a selected microscopic region, the unique phenomena above mentioned can be obtained to stimulate an objective reaction without affecting external surrounding. Moreover, focusing a high energy light beam into small region results in the production of an extremely intense electric field that is almost equal to the field inside a hydrogen atom. Such an intense femtosecond pulse synthesis of metal and alloy NPs are growing rapidly. However, solid-solution alloy NPs has been rarely reported. The main advantage of alloys over their pure metals is the controllability of properties by manipulating its composition. In this dissertation, the syntheses of pure Rh NPs, solid-solution binary Rh-Pd, Rh-Pt and ternary Rh-Pd-Pt alloy NPs were studied using highly intense femtosecond laser irradiation of metal ion solutions. The pure

metal and alloy NPs were facilitated through the reduction of metal ions by transient species, which were easily produced by the optical decomposition of water molecules through multiphoton absorption and avalanche ionization of solvent molecules in a high-energetic optical field and were abundantly present in the solution. All-proportional solid-solution alloy NPs were obtained in this study due to strong reducing power of the reactive species. The fabricated particles had been characterised through UV-vis. spectroscopy, transmission electron microscopy, X-ray diffraction technique, HAADF STEM-EDS mapping, X-ray photoelectron spectroscopy to determine the size, crystal structure, composition, electronic state as well as the stability of the particles. Moreover, the catalytic CO oxidation of Rh, Pd, Pt and their binary Rh–Pd, Rh–Pt and ternary Rh–Pd–Pt alloy NPs supported with γ -Al₂O₃ were also measured. The key point of each chapter is summarized as follows.

In Chapter 1 [Introduction], the potential and application of colloidal noble metal and alloy NPs were briefly overviewed, especially the importance of composition-controlled alloy NPs was high-lighted as a reminder that the physical and chemical properties of alloy NPs can be easily controlled by tuning its compositions. Moreover, femtosecond laser assisted synthesis was briefly discussed including the advantage for the formation of solid-solution alloy NPs.

Chapter 2 [Synthesis of NPs through Femtosecond Laser Irradiation of Aqueous Solutions] dealt with the interaction of femtosecond laser pulses with a liquid material used as a target for NPs synthesis. Special attention has been paid to discuss about the nonlinear optical effects e.g. the multiphoton absorption and the avalanche ionization, and the production of transient species in water. Moreover, the instruments for the characterization of the metal and alloy NPs were also reviewed.

In Chapter 3 [Synthesis of Pure Rh NPs and binary Rh–Pd and Rh–Pd Alloy NPs], Rh NPs had been successfully fabricated simply by irradiating the corresponding precursor solution by femtosecond laser pulses. The effect of concentrations on the formation of NPs was examined, and it was found that lower concentration of solution (2.5×10^{-4} M) is preferred to form the NPs with smaller size and more uniform size distribution. Based on the result obtained in the laser irradiation of Rh solution, solid-solution Rh–Pd and Rh–Pt NPs were fabricated through femtosecond laser irradiation of mixed solutions without any reducing agents. The XRD peaks of NPs obtained in the mixed solutions with different ratios of Rh–Pd and Rh–Pt ions monotonically shifted from the position of pure Rh to that of Pd or Pt depending on the molar fractions. Size of the fabricated particles was in the range of 10 to 20 nm and the composition was fully tunable in accordance with the molar fraction of the solutions. This strongly indicated the formation of all-proportional solid-solution binary alloy NPs in spite of the immiscibility of elements. This was achieved by the co-reduction process due to the strong reducing power of solvated electrons and hydrogen radicals produced by high-intensity femtosecond laser irradiation of solutions. Then, most of the ions were consumed by the reduction and the particles ceased growing after they became several nanometers in size, and homogeneous alloy was formed through inter-diffusion between two elements promptly after the reduction of metal ions.

Synthesis of solid-solution Rh–Pd–Pt ternary alloy NPs using high intensity femtosecond laser irradiation of mixed solution of metal salts was performed in Chapter 4 [Synthesis of Rh–Pd–Pt Solid-Solution Ternary Alloy NPs in Aqueous Phase]. In this chapter, solid-solution Rh–Pd–Pt ternary alloy NPs with well-controlled compositions had been demonstrated through femtosecond laser irradiation of a mixed solution of metallic ions without any pre-added reducing agents. The structure of fabricated NPs was confirmed by diffraction techniques. The crystalline nature of alloy NPs was also confirmed through HR-TEM measurement. According to EDS analysis, elemental composition of individual NP was almost the same as the initial feeding ratio of ions in the mixed solutions. The electronic state of each element in alloy NPs was confirmed to be pure metal by XPS measurement. The structural studies of Rh–Pd–Pt NPs suggested that the demonstrated technique has potential to open up a new dimension for the fabrication of multimetallic NPs over three elements which has well-controlled properties for

practical use in various fields.

In Chapter 5 [All-Proportional Solid-Solution Rh–Pd–Pt Alloy NPs by Femtosecond Laser Irradiation of Aqueous Solution with Surfactants], the formation of solid-solution ternary Rh–Pd–Pt alloy NPs by femtosecond laser irradiation of aqueous solution in the presence of PVP or citrate as a stabilizer was intensively studied. It was found that the addition of surfactant (PVP or citrate) significantly contributed to reduce the mean size of fabricated particles to less than 10 nm depending on the surfactant applied, which was much smaller than that of particles fabricated without any surfactants (~20 nm, Chapter 4). The dispersion state as well as the stability of the colloids were also improved. Though the composition of Rh–Pd–Pt alloy NPs significantly reflected the feeding ratio of the ions in the mixed solution with citrate, Pt-rich NPs were formed in the solution with PVP, because PVP acted as a reducing agent as well as a dispersant during particle formation. These results demonstrated not only the solid-solution alloy formation but also the controllability of size and composition of the fabricated NPs which can be applied to practical use.

Catalytic activity of metal and alloy NPs was demonstrated in Chapter 6 [Catalytic Activity of Metal and Alloy NPs]. Catalytic CO oxidation was carried out for catalysts of their metal and alloy NPs. Rh, Pd and Pt NPs and their binary and ternary solid-solution alloy NPs fabricated by laser irradiation of solutions were supported nicely on γ -Al₂O₃ matrix through two step process for catalytic application. Catalytic activity of pure Rh NPs was better than that of pure Pd and Pt NPs. Moreover, catalytic activity of binary Rh–Pt was better than that of intermediate between Rh and Pt. Although the catalytic stability was much improved by alloying, the catalytic activity was not so much enhanced in comparison with that of Rh and Pd. This might be due to a uniform local structure. However, the enhancement of catalytic activity of binary Rh–Pd alloy NPs was confirmed after heat-treatment probably due to the introduction of defect sites in the alloy NPs.

In summary, this thesis is the first demonstration of significant findings and advances about the synthesis of solid-solution binary Rh–Pd, Rh–Pt and ternary Rh–Pd–Pt alloy NPs by the use of interaction of femtosecond laser pulses with liquid materials. Moreover, the synthesized metal and alloy nano-particles were used as catalysts and the origin of enhanced catalytic activity of multimetallic NPs were discussed in terms of local structure. I believe that this research gives great contributions not only to the research fields but to the industrial applications.

論文審査結果の要旨

貴金属ナノ粒子は触媒などへの応用を目指した研究・開発が行われているが、触媒活性の向上が期待される多元系合金粒子に関する研究は少なく、簡便で環境負荷の少ない微粒子作製方法の開発は喫緊の課題であるとされている。本論文は、フェムト秒パルスレーザー光を溶液中に集光して作り出した高強度レーザー場を反応場とする新しい反応プロセスを適用し、Rh をベースとした Pd および Pt との 2 元系および 3 元系の合金ナノ微粒子を作製し、組成と構造の特性評価に加え、触媒活性の比較を行ったものである。

第 1 章は序論であり、本研究の背景と目的を述べている。

第 2 章では、フェムト秒レーザー光と物質との相互作用および微粒子作製法の基本的特徴について述べている。

第 3 章では、まず Rh イオン水溶液を試料として、高強度レーザー場におけるナノ粒子作製に続き、Pd および Pt イオンとの混合液を用いた Rh ベースの 2 元系合金ナノ粒子を作製し、ナノ粒子が固溶体であることと組成を制御できることを明らかにしている。

第 4 章では、Rh-Pd-Pt 3 元系合金ナノ粒子の作製を行い、2 元系の場合と同様に、ナノ粒子が固溶体であることと組成を制御できることを明らかにしている。

第 5 章では、界面活性剤を加えた貴金属イオン混合液へのフェムト秒レーザー照射によるナノ粒子作製を行い、粒子径とその分散の制御が可能であることを明らかにしている。

第 6 章では、一酸化炭素の酸化反応に対する、2 元系および 3 元系ナノ粒子の触媒活性を測定し、合金化による触媒活性の向上と、繰返し使用に対する劣化の抑制効果を明らかにした。また、熱処理を施したナノ粒子の触媒活性の増強効果を見出した。

第 7 章は総括である。

以上要するに、本研究は、高強度レーザー場を用いて Rh をベースとした Pd および Pt との 2 元系および 3 元系合金ナノ粒子の作製と特性を評価したものであり、固溶体合金ナノ粒子作製とその組成制御を世界に先駆けて報告したものである。これらの成果は、合金ナノ粒子における原子レベルでの組織と組成制御の重要性を明らかにしたものであり、材料工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。