

Synthesis of Noble Metal Nanoparticles in Intense Laser Field

著者	YULIATI HERBANI
号	56
学位授与機関	Tohoku University
学位授与番号	工博第4540号
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	ユリアティ ヘルバニ
氏 名	YULIATI HERBANI
授 与 学 位	博士 (工学)
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指 導 教 員	東北大学教授 佐藤 俊一
論 文 審 査 委 員	主査 東北大学教授 佐藤 俊一 東北大学教授 川崎 亮 東北大学教授 鈴木 茂

論 文 内 容 要 旨

In our modern society, the nanosciences have recently evolved as a major research direction, resulting from enormous ongoing efforts to reduce almost everything becomes a nanometer size. However, the tools and processes employed are those currently used for microsystems. A new approach is needed. The classic top-down approach should be replaced by the bottom-up approach. This strategic move would synchronize with existing areas of nanosciences such as opto-electronics, sensing, medicine and catalysis. The bottom-up approach is preferable because the size, shape and composition of nanomaterials can be fine-tuned much easily. The end products by the bottom-up method are generally referred to as “colloidal nanoparticles”, because the particles are formed in the presence of liquid solvent at the expense of ions mixed with some additives that keep the nanoparticle stable for months or longer. Once colloidal nanoparticles 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 the engineering and tailoring of nanoscale structures for specific technological applications.

To synthesize colloidal metal nanoparticles, the bottom-up method is the most appropriate method considering the nature of synthesis itself that relies on the reduction process of chemical precursors in the solution using reducing agents. The reducing agents can take many forms such as chemicals, mechanical wave (ultrasound) and electromagnetic waves. Regardless of the type of reducing agent used in the system, the important key factor for the bottom-up synthesis is the continuous availability of electrons in the system which guarantees the reduction process to persist. Several methods have been briefly reviewed in terms of the production of metal nanoparticles. All of them have different advantages and disadvantages, and it is difficult to find a method that fulfills all the requirements such as the cleanliness, high volume toward mass production, monodispersivity, ultrashort reaction time, capability of fabricating any kind of metal nanoparticles, etc. The ultimate goal is to find a production route where single nanometer-sized particles can be obtained directly without further separation. There is also an increasing need to developed high yield, low cost, non-toxic and environmentally benign procedure for the synthesis of metallic nanoparticles. An alternative route that one can think of is the use of femtosecond laser. The formation of zerovalent metal atoms was facilitated through the reduction process by the solvated electrons and

transient species that are abundantly present in the solution as a result of the multiphoton excitation and ionization of solvent molecules. Having the property of light, synthesis of nanoparticle using femtosecond laser would be expected to possess the characters like highly spatial resolution, reaction selectivity, reaction controllability, and shape conversion via photoirradiation. These aspects can be obtained due to the flexibility of the femtosecond laser to be focused in selected and microscopic region, the capability to stimulate an objective reaction without affecting external surrounding, characteristics that allow us to start the reaction at any given time, and the highly intense electromagnetic field that can exclusively triggers a fragmentation or crystal reshaping of a nanoparticle during the prolong irradiation. Additionally, the femtosecond laser may provide the same quality of those synthesized by either synchrotron X-ray or γ -ray, considering that femtosecond laser can be focused into a very small region resulting in an extremely intense electric field that is about equal to the field inside a hydrogen atom. Direct implication of these characteristics to the nanoparticle synthesis is that the production of sub 5 nm particles is possible, in addition to the other promising aspects mentioned above. Furthermore, only a few reports are available so far on the nanoparticle synthesis using femtosecond laser irradiation, and thus, this synthesis route has not been fully explored yet. In this doctoral dissertation, the syntheses of pure, binary and ternary system of colloidal noble metal nanoparticles of Au, Pt and Ag were studied using highly intense femtosecond laser pulses. The essential point of every chapter is summarized as follows.

In **Chapter 1 [Introduction]**, basic definition of colloidal noble metal nanoparticle along with brief description of its properties and applications were overviewed as a reminder that nanoparticles could be fully functional if the engineer can control over the size, shape and composition. Depending on the type of reducing agent stored in the system (i.e. chemicals, mechanical and electromagnetic wave), some synthesis methods were briefly reviewed in terms of the production of metal nanoparticles. All of them have different advantages and disadvantages, and it is difficult to find a method that fulfills all the requirements such as the cleanliness, high volume toward mass production, monodispersivity, ultrashort reaction time, capability of fabricating any kind of metal nanoparticles, etc. The ultimate goal is to find a production route where single nanometer-sized particles can be obtained directly without further separation. There is also an increasing need to developed high yield, low cost, non-toxic and environmentally benign procedure for the synthesis of metallic nanoparticles. An alternative route that one can think of is the use of femtosecond laser.

Chapter 2 [Femtosecond Laser Induced Synthesis of Nanoparticles] dealt with the basic principle about femtosecond laser, especially its fundamental interaction with liquid as the main materials used in the nanoparticle synthesis. Multiphoton absorption and avalanche ionization of liquid water toward the production of transient species in water was also reviewed and the basic knowledge on handling the experiment of nanoparticle synthesis using femtosecond laser was also discussed.

In **Chapter 3 [Synthesis of Pure Au and Ag Alloy Nanoparticles]**, Au and Ag nanoparticles had been successfully fabricated simply by irradiating the corresponding precursors by femtosecond laser pulses. Addition of dispersant enhanced the formation of nanoparticles and contributed in making the particle size smaller. While Au nanoparticle was easily fabricated without any limit of ion concentration, Ag nanoparticles were able to be formed at the concentration larger than 3.0×10^{-2} M, while most of ions were still remained in the solution. This

might be attributed to the low reduction potential of free Ag^+ ions in water. The Ag atoms would be readily oxidized once moderate oxidizing molecules like hydroxyl radical were formed in the solution. However, the fabricated particles were confirmed to be pure Au and Ag without any oxidation state.

The synthesis of colloidal binary Au–Ag alloy nanoparticles using highly intense laser irradiation of the mixed solution of aqueous metal salts were performed in **Chapter 4 [Synthesis of Au–Ag Alloy Nanoparticles in Aqueous Phase]**. There were two batches of solution were prepared: (i) in low concentration and (ii) in the presence of ammonia without any dispersant. Some additional techniques to produce Au–Ag nanoparticle were also presented by utilizing the sequential irradiation of Au and Ag ions. The irradiation of physical mixture of monometallic Au and Ag nanoparticles prepared by femtosecond laser was also demonstrated.

In the first batch, despite the production yield was low, the Au-rich nanoparticles were formed due to the low reduction rate of Ag ions. The alloy formation was confirmed by the continuously shift of the absorption peak with varying Au molar fraction and by the appearance a single plasmon absorption band for all samples with different compositions of metal ion in the solution. HR-TEM images also exhibited the absence of core-shell structure. The electron transfer from co-reduced Au atoms to Ag ions was also considered as a factor that caused the formation of the Au-rich nanoalloys.

In the second batch, the addition of ammonia was found to enhance the formation rate of both Au and Ag nanoparticles, resulting in the formation of binary alloy particles with few-nanometer sizes at the end of the alloying process. The general trends in the plasmon peak with the increase of the Au molar fraction, i.e., the linear shifts of the plasmon peaks, the gradual increase in bandwidth and the decrease in the absorbance, were clearly observed and in a good agreement with the absorption features suggested in Mie's theory, implying that the nanoalloys were not in a segregated phase but homogenous. Using EDX area analysis, the elemental compositions in the nanoparticles were also found to be almost the same as the molar ratios of ion in the initial solution. HR-TEM images showed no phase segregation and no core-shell type structure, although most particles were not merely a single crystal but polycrystalline and possessed defect plane and stacking faults. The synthesis of AgCl-free Au–Ag alloy nanoparticles was also confirmed by XRD analysis when the irradiation time was prolonged up to 2 hours.

The sequential irradiation of the solution with 50 % ratio of Au content, both in the order of Au ion – Ag nanoparticles and vice versa, resulted in the alloy formation, which was confirmed by the same position of SPR peak for both cases. The alloy formation was also achieved by the irradiation of physical mixture of Au and Ag nanoparticles.

In **Chapter 5 [Synthesis of Au, Ag and its Alloy Nanoparticles in Organic Phase]**, pure Au, Ag and their binary nanoparticles were performed in normal hexane. Highly concentrated metal nanoparticles with narrow size distribution were achieved. Not only pure Au and Ag nanoparticles but also the Au–Ag bimetallic particles in hexane are very fine with the particle size of 2 – 5 nm, well separated each other and essentially near-monodisperse. The Au–Ag binary system was confirmed to be solid solution alloy from the appearance of single plasmon band whose position was between those for monometallic nanoparticles.

The synthesis of ternary Au–Pt–Ag alloy nanoparticles with variable compositions was demonstrated in **Chapter 6 [Synthesis of Ternary Au–Pt–Ag Alloy Nanoparticles]**. In the presence of ammonia and PVP, the

ternary particles have a small size (~5 nm). The structure of the alloyed nanoparticles was *fcc* and the composition was close to that in the mixed ion solutions. We also found that the binary immiscible system of Au–Pt and Ag–Pt nanoparticles could also be synthesized as a form of homogenous alloy nanoparticles using the same method.

In **Chapter 7 [Formation Kinetics of Nanoparticles in Highly Intense Laser Field]**, the qualitative study on the formation kinetics of binary Au–Ag nanoparticles in the presence of ammonia was performed by monitoring the evolution of the absorption spectra during laser irradiation. The nucleation and growth stages in the formation process of pure Au and Ag particles, and its binary nanoalloys by photoreduction induced by femtosecond laser can be identified. The effects of additives, the elemental composition and the laser pulse energies on the formation kinetics were also studied. It was found that the formation rate of pure Au and Ag nanoparticles were enhanced in the presence of ammonia. In the binary nanoparticles, the formation behavior exhibited the dynamic process of the particle growth where the two elements might compete each other. The composition ratios of the precursor in the mixed system did not significantly affect the formation behavior, except for the time needed for the completion of the reduction. The more Ag content the solution system had, the more rapid the formation process would be finished due to the high formation rate of Ag nanoparticles in the presence of ammonia. Nucleation stage in the formation process of the binary Au–Ag nanoparticle was found to be shorter than 2 minutes. Furthermore, in the early stage of the growth process, the particles were large and Ag-rich as confirmed by the EDS analysis. When the high laser energy and long irradiation were applied, the alloy nanoparticles were produced more uniformly in the particles size. Nevertheless, this qualitative study showed that the mechanism underlying the formation of metal nanoparticles in photoreduction process by femtosecond laser constituted three elementary phases: (1) nucleation stage ($t < 2$ min), (2) growth stage ($t = 2 - 20$ minutes) and the ripening stage (size reduction stage) by the laser ($t > 20$ minutes).

As shown in this thesis, new interesting findings and advances about the synthesis of pure and alloyed noble metal nanoparticles have been revealed, mainly by exploiting the interaction of femtosecond laser pulses with liquid. This synthesis route provides an easily and reproducible synthetic approach. Thus, it is considered that this study is useful and worthwhile for actual application in industry as well as from the academic view point.

論文審査結果の要旨

これまでに様々な微粒子作製方法が開発されているが、シングルナノオーダーの微粒子を環境負荷が少なく、かつ安全に作製できる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提起し、貴金属のシングルナノ微粒子、さらに2元系および3元系の貴金属合金ナノ微粒子の作製を実現し、また局在表面プラズモン共鳴を利用して複雑な合金微粒子形成のダイナミクスを明らかにしたものである。

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、金および銀イオンの水溶液を試料として、高強度レーザー場における金および銀の微粒子作製を行い、シングルナノメートルオーダーの微粒子が合成できることを明らかにしている。

第4章では、金および銀イオンの混合水溶液を試料として高強度レーザー場を用いた微粒子作製を行い、局在表面プラズモン共鳴による吸収スペクトル解析から、微粒子が全率固溶の合金であることを明らかにしている。また、アンモニア添加により、微粒子生成効率が向上することを見出している。

第5章では、イオン輸送法を適用して、水溶液中の貴金属イオンを有機溶媒中へ高濃度で移動させ、これに高強度レーザー場を用いるプロセスを適用して微粒子作製を行い、高い微粒子生成効率と小さな粒度分布を実現できることを明らかにしている。

第6章では、金、銀およびプラチナイオンの混合水溶液を試料として高強度レーザー場を用いた微粒子作製を行い、3元系の合金微粒子作製が実現できることを明らかにしている。

第7章では、金および銀イオンの混合水溶液を試料とする高強度レーザー場による微粒子作製プロセスに対して、局在表面プラズモン共鳴による吸収スペクトルの実時間測定を行い、合金微粒子プロセスが核生成、成長および熟成の段階を有することを明らかにしている。

第8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シングルナノ貴金属微粒子および合金微粒子の作製に成功し、このプロセスが還元剤を全く必要とせず、また、常温常圧下で安全に実施できることを世界に先駆けて実証したものである。これらの成果は、環境負荷が少ない新しいシングルナノ貴金属合金微粒子の作製プロセスの可能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。