Vapor-phase synthesis of bimetallic plasmonic nanoparticles

Naomi Sakono*†, Kazuki Omori*, Koki Yamamoto*, Naru Ishikuro*, Masafumi Sakono**

* Department of Applied Chemistry and Chemical Engineering, National Institute of Technology, Toyama College, 13 Hongo, Toyama, Toyama 939-8630, Japan

** Department of Applied Chemistry, Faculty of Engineering, University of Toyama, 3190 Gifuku, Toyama, Toyama 930-8555, Japan

Corresponding author: Naomi Sakono

Department of Applied Chemistry and Chemical Engineering, National Institute of Technology, Toyama College, 13 Hongo, Toyama, Toyama 939-8630, Japan

E-mail: nsakono@nc-toyama.ac.jp

Fax: +81-76-492-3859; Tel: +81-76-493-5402
Abstract

Regulating the nanostructure of composite nanoparticles is essential for making them suitable for various applications. In general, the chemical reduction method is employed for the preparation of metal nanoparticles in the liquid phase. However, complicated techniques are required to control the nanostructure during particle synthesis. The evaporation/condensation method is used for synthesizing nanoparticles in the vapor-phase. Although this method produces impurity-free particles without aggregation, very few studies have been carried out on the synthesis of composite particles in the vapor-phase. In this study, we synthesized composite nanoparticles in the vapor-phase by using the evaporation/condensation method. The results showed that bimetallic nanoparticles are produced by the evaporation/condensation method. Moreover, it was indicated that the nanostructure of the synthesized nanoparticles is influenced by the order of the electric furnace with different temperature.

Keywords: Plasmonic nanomaterial, nanoparticle synthesis in vapor phase, evaporation/condensation method, nanostructure
Introduction

Composite nanoparticles composed of multiple metals are used for catalysis and biosensor applications. Nanostructures of bimetallic particles are classified as heterogeneous, core-shelled, and alloyed structures. Although bimetallic nanoparticles exhibit optical and electromagnetic properties different than those of monometallic nanoparticles, their properties significantly depend on their nanostructure patterns. Therefore, controlling the nanostructure of composite nanoparticles is imperative.

The chemical reduction method is generally employed for the preparation of metal nanoparticles in the liquid phase. In this method, nanoparticles are produced by adding a reducing agent to a metal precursor-containing solution. In order to control the particle growth, protective reagents such as polyvinylpyrrolidone (PVP) and polyethylene glycol are employed. Although composite nanoparticles can be obtained by the reduction of solubilized multiple metal precursors, complicated techniques are required to regulate the nanostructure of composite materials.

Over the past few years, the production of nanostructures in the vapor phase has gained significant attention. The evaporation/condensation method is used to produce nanoparticles in the vapor phase. In this method, nanoparticle synthesis is achieved by the reassembly of metal atoms obtained by the evaporation of bulk metal. Particle aggregation is less likely to occur during the vapor-phase synthesis than during the liquid phase synthesis. Hence, in the vapor synthesis method, the addition of protective agents is not required. In addition, the vapor-phase synthesis method produces impurity-free particles without using any reducing agent. In our previous studies, we collected aerosol particles in a PVP-dissolved solution without agglomeration by passing the carrier gas containing the generated particles through it, demonstrating that aerosol nanoparticles can be collected in aqueous solutions. Therefore, the evaporation/condensation method is an efficient approach to produce industrial catalysts.
However, very few reports are available on the synthesis of composite particles in the vapor phase, except for preliminary studies on the ion spray method.\textsuperscript{10}

In this study, we prepared composite nanoparticles in the vapor phase using the evaporation/condensation method. The nanostructures and optical properties of the composite metal nanoparticles were investigated. Nanoparticle synthesis was carried out in a quartz tube equipped with two electric furnaces. Metals were evaporated at melting temperatures adjusted by each of the electric furnaces under the flow of a carrier gas. The carrier gas was passed through an aqueous solution containing PVP, and the vapor phase generated particles were collected. The results confirmed the successful preparation of alloyed and core-shelled composite nanoparticles using the evaporation/condensation method.

**Experimental**

*Preparation of nanoparticles in vapor phase.*

As shown in Figure 1, we fabricated a nanoparticle synthesis device consisting of two electric furnaces (Co., Ltd. Isuzu Seisakusho) attached to a quartz tube ($\phi = 18$ mm). The electric furnaces were labeled as furnace 1 and furnace 2 from the upstream side. Inside the quartz tube, nitrogen was flown from the upstream at a rate of 2 L/min. The metals (Ag, Au, 1 g) were placed on each side of the tube furnace. The temperatures of the Ag and Au electric furnaces were set at 1100 °C and 1500 °C, respectively. We confirmed that the temperature of both furnaces were sufficient to produce gas-born nanoparticles (data not shown). Our preliminary results suggest that furnace temperatures of Ag and Au should be $>900$ and $>1300$ °C, respectively. Nanoparticles synthesis were conducted under atmospheric pressure.
Characterization of prepared nanoparticles.

The vapor phase nanoparticles were collected onto a collodion-coated Cu grid (Nissin EM Co.) installed in the quartz tube (downstream) for 10 min. The nanoparticles on the grid were observed using a transmission electron microscope (TEM, H-7650, HITACHI) operating at 100 kV. The size distribution of the synthesized particles (for more than 100 particles) was analyzed using the TEM. Elemental mapping and line-scan analyses were carried out using an STEM (JEM-ARM 200F, JEOL) equipped with EDS. Accelerating voltages of 300 (for elemental mapping analysis) and 200 kV (for line-scan analysis) were used.

Collection of vapor-phase nanoparticles into liquid-phase.

The gas-born nanoparticles were collected in the liquid phase according to the procedure used by us in our previous study. The PVP-dissolved aqueous solution (0.125 g/L) used for collecting the nanoparticles was placed at the downstream of the quartz tube. The bubbling of the nitrogen gas released from the quartz tube was carried out for 3 h. The absorbance of the collected nanoparticles was recorded over the wavelength range of 300–700 nm using an ultraviolet-visible (UV-Vis) spectrophotometer (UV-2450, Shimadzu).

Results and Discussion

The nanoparticles obtained when Ag and Au were placed in the quartz tubes of furnaces 1 and 2, respectively were labelled as Ag-Au while those obtained when Au and Ag were placed in the quartz tubes of furnaces 1 and 2, respectively were labelled as Au-Ag. The shape and diameter of the nanoparticles were examined by TEM observation. Figure 2 shows the TEM images and size distributions of the Ag-Au and Au-Ag nanoparticles. Spherical nanoparticles were observed in
both the samples. The mode value of the size of the Ag-Au nanoparticles was about 3 nm, and the
distribution was 1–13 nm. The Au-Ag nanoparticles showed similar size distribution and particle
sizes. No significant difference was observed in the size distributions of the Au-Ag and Ag-Au
nanoparticles. Therefore, the size of the nanoparticles was not affected by the order of furnaces
linked to the quartz tube.

The elemental compositions of the nanoparticles were investigated by carrying out their mapping
and line-scan analyses using STEM. Figure 3 shows the mapping and line-scan analysis results
of the Ag-Au nanoparticles. The mapping image of the nanoparticles (Figure 3 (a)) showed bright
spots corresponding to Au and Ag atoms in the same particle, suggesting that the synthesized
nanoparticles consisted of both the elements. The elemental composition result revealed that the
nanoparticles contained more Au than Ag. The distribution state of the constituent elements was
examined by the line-scan analysis of the nanoparticles. The line-scan analysis revealed the
presence of both Au and Ag in the nanoparticles (Figure 3 (b)). Moreover, both the elements were
evenly distributed on the particles. The line-scan analysis confirmed the abundance of Au in the
nanoparticles. An EDS analysis also indicated that the mole fraction of Au was estimated as 80%
in Ag–Au nanoparticles. This number is consistent with the mapping analysis results. The even
distribution of both the elements suggests that the synthesized nanoparticles showed an alloyed
structure not a core-shelled structure.

Then, the mapping and line-scan analyses of the Au-Ag nanoparticles were carried out. The
mapping analysis (Figure 4 (a)) results showed that both Ag and Au elements were present in the
Au-Ag nanoparticles. This indicates that the Au-Ag nanoparticles were bimetallic. The line-scan
analysis results revealed that the Au-Ag nanoparticles showed nonuniform atomic distribution of
Au and Ag (Figure 4(b)). The mole fraction of Au in Au–Ag was estimated as 7% from an EDS
analysis. These results indicate that the Au–Ag nanoparticles were core-shell type composite
nanoparticles composed of Ag shell and Au core, suggesting that the order of the furnaces attached to the quartz tube significantly affected the nanostructure of composite particles. The optical properties of the nanoparticles were evaluated by measuring their absorbance using UV-Vis spectroscopy. The vapor phase generated particles were collected by pass through an aqueous collection solution containing PVP. Figure 5 shows the absorbance spectrum of the collection solution. The surface plasmon absorption peaks of Ag and Au mono atomic nanoparticles were observed at 398 and 525 nm, respectively. The solution containing the Ag–Au particles showed a single absorption peak at 509 nm. The alloy nanoparticles composed of Ag and Au showed an absorbance wavelength intermediate to those of Ag and Au monometallic nanoparticles, depending on the ratio of the constituent metal atoms\textsuperscript{14}. The shape of spectrum of the alloy-type nanoparticle was consistent with the 80% of Au mole fraction, which is in agreement with our result. The absorption peaks of Au–Ag appeared at 425 and 567 nm, which are close to the characteristic peaks of Ag and Au nanoparticles, respectively. For the core-shell type nanoparticles, two peaks corresponding to the constituent metals were observed, and the absorption wavelength shifted to the longer wavelengths\textsuperscript{15}. Thus, the spectrum of Au–Ag nanoparticles is similar to one of core-shell type nanoparticles. These nanostructures estimated by the UV-Vis results were consistent with the elemental analysis results (Figures 3 and 4). Hence, all results indicate that the nanostructure of nanoparticles prepared in this study differed depending on order of electric furnace.

From the above results, we succeeded in the highly selective synthesis of nanoparticles with different nanostructures. An estimated mechanism is shown in Figure 6. The evaporation elements generated in furnace 1 (named as Element 1) were transferred to furnace 2 by the flow of nitrogen gas. The behavior of Element 1 is considered to change depending on the temperature of furnace 2. When the temperature of furnace 2 is lower than the evaporation temperature of Element 1,
Element 1 is thought to be reassembled in furnace 2. Therefore, the evaporation element generated in furnace 2 (Element 2) might be used to generate core-shell nanoparticle on the aggregates of Element 1. In contrast, when the temperature of furnace 2 is sufficient to maintain the evaporation state of Element 1, the mixing of Element 1 and Element 2 in this furnace will result in the production of alloy-type nanoparticles.

Conclusions

In this study, we prepared bimetallic nanoparticles using an evaporation/condensation method. Two kinds of metals were installed in a tube furnace using a quartz tube equipped with two electric furnaces. The mapping and line-scan analysis results revealed that the nanostructure of synthesized nanoparticles was influenced by order of the electric furnaces. The UV-Vis results also showed that the optical properties of the nanomaterials synthesized in this study were comparable to those of alloy and core-shell type nanoparticles. In recent years, composite nanoparticles have been reported to be used not only as catalysts\(^{16}\) but also as sensing elements for small molecule detection\(^{17-19}\). The production of particles with different nanostructures may significantly contribute to enhancing electrochemical analysis techniques.

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**Figure captions**

Fig. 1 Schematic of the experimental setup used in this study

Fig. 2 TEM image of the (a) Ag-Au, (c) Au-Ag nanoparticles and size distribution of the (b) Ag-Au, (d) Au-Ag. Scale bar indicates 50 nm.

Fig. 3 STEM images of the Ag-Au nanoparticles. (a) elemental mapping analysis, (b) line-scan analysis (red and blue lines show Ag and Au, respectively.). Scale bar indicates 10 nm.

Fig. 4 STEM images of the Au-Ag nanoparticles. (a) elemental mapping analysis, (b) line-scan analysis (red and blue lines show Ag and Au, respectively.). Scale bar indicates 10 nm.

Fig. 5 Absorption spectra of Ag, Au, Ag-Au, and Au-Ag nanoparticles.

Fig. 6 Estimated mechanism of generating Ag–Au and Au–Ag nanoparticles. Upper panel shows the case when furnace 2 temperature is lower than the evaporation temperature of Element 1. Lower panel the case when furnace 2 temperature is higher than the evaporation temperature of Element 1.

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Figure 1
Figure 2
Figure 3
Figure 4

(a) (b)

Dark field Ag

Au Merge

(b)

Intensity vs Distance [nm]
Figure 5
Figure 6

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