In-Situ Observation for Formations of Gold Micrometer-Sized Particles in Liquid Phase Using Atmospheric Scanning Electron Microscopy (ASEM)§1

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In this report, we present a novel method to produce micrometer-sized gold particles by dissolving and recovering gold from a dimethyl sulfoxide/hydrochloric acid (DMSO/HCl) solution containing copper (II) chloride (CuCl2) and sodium chloride (NaCl). It was reported that spherical or confeito-like particles can be formed depending on the concentrations of dissolved gold and Cl− ions in the solution. In this paper, in-situ observation of gold particle formation in the solution phase was conducted using atmospheric scanning electron microscopy (ASEM). An electron-permeable window made of a pressure-resistant silicon nitride (Si3N4) film (100 nm-thick), was set at the bottom of the open ASEM sample dish, which facilitated the projection of electron beams from underneath the sample. This structure of ASEM enabled us to observe dynamic phenomena in liquid or gas phase under atmospheric pressure in real time. It was found during the in-situ observation that all of the particles formed were confeito-like in shape, which was different from the expected particle morphology.

Keywords: atmospheric scanning electron microscopy (ASEM), gold, in-situ observation, particle formation

1. Introduction

In recent years, due to environmental implications, the recovery of precious metals such as gold from used electric and electronic devices is highly emphasized1,2). In the recent past, we have developed a noble metal recovery process using dimethyl sulfoxide (DMSO) solvent containing copper halide. In this process, gold dissolves at a standard pressure under a mild atmosphere of about 343 K, and subsequently can be precipitated and recovered by the addition of an aqueous acid solution. This process enables us to use these solutions repeatedly, leading to the development of an economical recycling process with minimal environmental impact3,4). Furthermore, gold recovery by this liquid-phase reduction method is easy to operate5), along with the possibility of obtaining gold particles with confeito-like or spherical shaped micrometer-sized particles, depending on the reduction conditions such as the concentration of gold and chloride ions. Moreover, the precipitation time for the liquid-phase reduction of gold can be readily controlled from 1 to 30 min, and the produced particles can be observed by scanning electron microscopy (SEM). Thus, the gold particles were formed through nucleation and particle growth, and it is also suggested that the latter stops when the reduction time reaches around 30 min6). In our previous work7,8), we reported the liquid-phase reduction of gold, and subsequent filtering and drying of gold particles. However, by utilizing a conventional SEM, the state of the gold particles or the particle growth kinetics could not be observed directly.

In this paper, we report the successful formation of micrometer-sized gold particles by the liquid-phase reduction method using a DMSO solvent and aqueous hydrochloric acid solution. In addition, in-situ observation of gold particle formation using atmospheric pressure scanning electron microscopy (ASEM) is also reported.

ASEM is an electron microscope jointly developed by The National Institute of Advanced Industrial Science and Technology (AIST) and Nippon Denshi (JEOL), Ltd. This is accomplished by the use of a dish (ASEM dish) with a thin silicon nitride (Si3N4) film placed at the bottom of an inverted scanning electron microscope. In addition, the electron beam detector under the dish can be kept in a vacuum state, while the upper part of the dish can be opened to atmosphere7,8) (Fig. 1), thereby providing venues to observe samples in open air as well as underwater.

Because of its versatility and capability to observe in liquids and at atmospheric pressure in high resolution, ASEM is expected to be applied in medical fields such as for the observation of cellular tissues9,10). In addition to the use in biological fields, ASEM is used in diverse fields, including in energy and materials, such as for the in-situ observation of

![Fig. 1 Schematic diagram of the ASEM system.](image-url)
electrochemical reactions in the electrolyte in high resolution\(^8,11\).

In this paper, we intend to study the mechanism and growth rate of micrometer-sized gold particles by conducting an *in-situ* liquid-phase reduction from a DMSO solvent containing copper chloride and gold, and aqueous hydrochloric acid solution, and subsequent observations by ASEM.

2. Methods

2.1 Preparation of solvent

In this study, precipitation experiments of gold particles were carried out by using two solvent combinations that are expected to precipitate spherical and confeito-like gold particles\(^6\). The prepared solvents are shown in Table 1. Gold was initially dissolved using DMSO solvents containing CuCl\(_2\) and NaCl at 343 K, and the temperature was then decreased to room temperature, i.e. at around 298 K. These solvents will be referred to as "DMSO solvent containing gold" hereafter. Next, aqueous solutions of HCl and NaCl were prepared (these solvents will be referred to as "hydrochloric acid aqueous solution" hereafter). The two solvents were mixed at a volume ratio of 1:1 to precipitate gold. Figure 2 shows the mapping of the gold and chlorine ion concentrations, as well as the shape of the gold particles that are expected to be formed on mixing the two solvents.

For further confirmation, gold was subjected to liquid-phase reduction by using a previously reported solvent system. The particles were then filtered, washed, and dried by the same technique as reported before\(^6\). Finally, the shape of the particle of precipitation was observed using SEM (JSM-6510A).

### Table 1 Solvents used in this work.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>DMSO solvents containing Au</th>
<th>HCl aqueous solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.40 M CuCl(_2) 0.20 M NaCl</td>
<td>0.029 M 0.70 M HCl</td>
</tr>
<tr>
<td>2</td>
<td>0.20 M NaCl</td>
<td>0.059 M 1.0 M HCl</td>
</tr>
</tbody>
</table>

2.2 Production of micrometer-sized gold particles and operation of ASEM

50 μL of DMSO solvent containing gold was taken with a micropipette and dropped on the Si\(_3\)N\(_4\) thin film of the ASEM dish. The solvent was focused in this state. Next, the DMSO solvent containing gold on the Si\(_3\)N\(_4\) film was sampled with a micropipette, and was mixed with 50 μL hydrochloric acid aqueous solution previously collected in an Eppendorf tube, to initiate the liquid phase reduction of gold. The solution was then quickly returned to the ASEM dish and was observed through the ASEM. By using this sample preparation technique, droplets of approximately 2 mm of height and 4 mm of diameter were formed on the ASEM dish.

The accelerating voltage of the electron beam was 20 kV. Observations were recorded by both video and still images. The videos were recorded at a magnification of 3,000x, with an interval of 0.5 s (2 frames/s), while the still images were taken at magnifications of 3,000–30,000x.

3. Results and Discussions

The gold particles were observed for 60, 120, 180, and 300 s after the addition of hydrochloric acid aqueous solution to the DMSO solvent containing gold, as shown in Experiment No. 1 in Table 1, and the results are depicted in Fig. 3 (a)–(d). Both the picture as well as the video was taken from the same location (area) using ASEM. It was found that gold particles with a size of about 1 μm had already formed after 60 s of mixing the solvents, and the number of the particles were observed to increase over time.

Figure 4 shows a still image taken at a magnification of 3,000x after 27 min. At this time, the formation of new particles was not observed, indicating the completion of particle production. In ASEM, observation is only possible to about 2 μm from the film at an acceleration voltage of 20 kV\(^7,11\) thereby limiting the observation of the particles in the upper layer of the ASEM dish. In addition, it should be noted that small particles constantly sway in the liquid due to Brownian motion, hence observation may not be possible\(^8\). Also, it was noted that the observed particles were not spherical, but rather were protruded with a particle size of about 1 μm.

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*Fig. 2* Shape sorting by the concentration of Cl- ion and dissolved gold (Ref. ?).
Figure 5 (a), (b) shows still images taken at a magnification of 30,000x after a time lapse of 37 and 60 mins, respectively. It is seen that the produced particles were confeito-like with sharp protrusions. While only some particles were shown in the photograph, the particles were of almost the same size, even when observed from other locations, indicating the absence of any additional particle growth.

As mentioned before, by using current experimental conditions, it has been shown in the previous report\(^6\) that liquid-phase reduction has resulted in the precipitation of spherical-shaped gold particles\(^6\). Accordingly, gold was precipitated using the same protocol using DMSO solvent and hydrochloric acid aqueous solution, and was subsequently filtered, washed and dried. The resulting precipitates were then observed with SEM, the micrographs of which are shown in Fig. 6. Even though the gold particles were almost spherical, protrusions remained at places indicated by arrows in the figure. While there were variations in the particle size, the maximum size of those particles was observed to cap at 5 \(\mu m\), indicating that the growth of the particles to be relatively larger than those observed in the liquid phase by ASEM. It is also possible that confeito-like particles that were produced by the liquid-phase reduction had bonded and deformed during filtration, washing and drying, and subsequently grew into larger spherical particles.

Next, the images of the gold particles produced by adding hydrochloric acid aqueous solution to the DMSO solvent containing gold as described in Experiment No. 2 of Table 1, were observed by ASEM, and the micrograph is shown in Fig. 7. This image was taken 46 min after the start of observation, and particle formation along with growth seemed to stop at this studied time. As the concentration of gold contained in the DMSO solvent used in Experiment No. 2 was about twice of that in Experiment No. 1, the diameter of the produced gold particles were also relatively larger (comparison using Fig. 4). As mentioned before, the range of observation in ASEM is limited to approximately 2 \(\mu m\) from the film; therefore, observing the entire particle is not possible. However, by inspecting the shadow cast by the particle, it can be concluded that the diameter had grown to the maximum of 5 \(\mu m\). In addition, the morphology of the particle was observed to be spherical, with a rough and non-smooth surface.

For confirmation, gold was precipitated using the same DMSO solvent and hydrochloric acid aqueous solution as described in Experiment No. 2. The particles were filtered, washed and dried, and the precipitates were subsequently observed with SEM. The SEM micrographs as seen in Fig. 8 clearly demonstrate the formation of confeito-like particles.

4. Conclusion

We have successfully performed in-situ observation of micrometer-sized gold particle formation through the liquid-phase reduction method using a DMSO solvent and
aqueous hydrochloric acid solution under atmospheric pressure by using ASEM.

It was observed that the micrometer-sized gold particles had already formed approximately 60 s after the start of the liquid-phase reduction, and it was further seen that the particle production and growth were complete in about 30 min. The particle size in the liquid phase was about 1 μm, and particles beyond this size were not observed. In the previous report, we observed that even in the regions where liquid-phase reduction was expected to produce spherical particles, in-situ observation demonstrated the formation of particles with a confeito-like shape. It is therefore hypothesized that these confeito-like particles produced in the liquid phase, subsequently changed into spherical particles after passing through the filtration, washing, and drying steps. The mechanism of the formation of spherical particles is, however, a subject that needs to be studied in the future.

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**REFERENCES**