Sonochemical decomposition of noble metal oxides and sonochemical alloying of gold–silver systems

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ABSTRACT

Recently, environmental problems, such as global warming, have become more severe; thus, there is a requirement to implement sustainable development goals in materials processing. In this study, we investigated a low-cost and environmentally-friendly sonochemical process for the synthesis of metal nanoparticles with large specific surface areas and catalysis effects. Au$_2$O$_3$ hydrate and Ag$_2$O were reduced to Au and Ag, respectively, at room temperature in a short time when irradiated with ultrasound in ethanol. Furthermore, when a mixed powder of Au$_2$O$_3$ hydrate and Ag$_2$O was irradiated in ethanol, Au–Ag alloys were obtained in only 10 min. This fast and environmentally friendly alloying technique, known as sonochemical alloying, is promising for alloy syntheses.

1. Introduction

Sonochemistry, which is the application of ultrasound in chemical reactions, has attracted considerable attention as ultrasound accelerates chemical synthesis and can achieve products that cannot be achieved using conventional methods. It allows us to create ecofriendly and economical processes [1–5].

On the other hand, metal nanoparticles (NPs) with large specific surface areas can be employed in various fields, such as catalysis and material synthesis [6,7]. To obtain such NPs, carbonyl compounds and chlorides have been investigated [8], but they are toxic and require the treatment of residual ions. Therefore, there is a requirement for low-cost and environmentally friendly processes. To that effect, the reduction of precious-metal oxides in ethanol (EtOH) at room temperature and atmospheric pressure has been investigated [9–11].

In this study, we investigated the reduction and particle growth of gold (III) oxide (Au$_2$O$_3$) hydrate and silver (I) oxide (Ag$_2$O) irradiated by ultrasound in EtOH. These materials were selected because Au and Ag NPs can be used as environmentally friendly catalysts in various fields [12–14] and a low-environmental-impact process can be obtained using metal oxides [15]. Furthermore, we investigated the synthesis of Au–Ag alloy NPs at low temperatures via ultrasonic irradiation of a mixed powder of Au$_2$O$_3$ hydrate and Ag$_2$O. We also investigated the difference between the reduction and particle-growth mechanisms of the single- and mixed-material powders.

2. Experimental

2.1. Ultrasound irradiation of EtOH

Fig. 1 shows a schematic of the device. EtOH degassed using ultrasound and untreated EtOH were added to 500-ml beakers and irradiated with ultrasound (BRANSON Digital Sonifier S-450D; frequency: 20 kHz; pulse wide: 1 s ON 1 s OFF; output: 20–100 W), and the temperatures were measured.

2.2. Ultrasonic irradiation of Au$_2$O$_3$ hydrate and Ag$_2$O

Fig. 2 shows a flowchart of the experimental procedure. Au$_2$O$_3$ hydrate and Ag$_2$O in the degassed EtOH were irradiated with ultrasound (BRANSON Digital Sonifier S-450D; frequency: 20 kHz; pulse wide: 1 s ON 1 s OFF; output: 100 W) at room temperature.

2.3. Ultrasound irradiation of mixed powder of Au$_2$O$_3$ hydrate and Ag$_2$O

Mixed powders (mass: 1 g; molar ratio (Au:Ag) = 1:3, 1:1, and 3:1) were prepared in EtOH (500 mL) and irradiated (frequency: 20 kHz; pulse wide: 1 s ON 1 s OFF; output: 100 W) at room temperature.

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Thereafter, the solution was dried, and the obtained samples were analyzed by X-ray diffraction (XRD, Rigaku, RINT-2000), X-ray fluorescence (XRF, JEOL, JSX-3200), field-emission electron microscopy (FE-SEM, ZEISS, LEO-1420), elemental dispersive X-ray (EDX, HITACHI, S-640EDX) analyses, and Thermogravimetry-Differential Thermal Analysis (TG-DTA, TA Instruments, Q600). Lattice constants were measured using Si as the internal standard in the range of $2\theta = 36 \sim 116^\circ$. Step scan mode was used, and data was refined by the least-squares method. TG-DTA was performed to determine the melting point. TG-DTA was performed using alumina as the reference material and at a heating rate of 10 °C/min.

3. Results and discussions

3.1. Ultrasonic irradiation effect on EtOH

Fig. 3 shows the temperature profile of EtOH during ultrasonic irradiation. The higher the ultrasound output, the higher the temperature increase rate. The temperature was saturated at approximately 337 K for both samples. The maximum temperature during cavitation is given by the specific heat ratio of the dissolved gas [16], but there was no difference in the temperature profiles of degassed and untreated EtOH. We infer that there was a small dissolved gas in the untreated EtOH, or the effect of dissolved gas was small. Otherwise, as another possibility, degassed ethanol was not degassed sufficiently, and degassed ethanol released gas as well as the untreated ethanol.

3.2. Ultrasound irradiation of Au$_2$O$_3$ hydrate and Ag$_2$O

3.2.1. Reduction of Au$_2$O$_3$ hydrate and Ag$_2$O by ultrasonic irradiation

Fig. 4 shows the XRD patterns of Au$_2$O$_3$ hydrate and Ag$_2$O after ultrasonic irradiation. Au$_2$O$_3$ hydrate was reduced to Au in 10 min, and Ag$_2$O was reduced to Ag in 110 min. The size of crystallites at the end of reduction was determined by the Scherrer equation. The crystallite size of Au was 12.1 nm and that of Ag was 15.9 nm. According to previous studies, the above reduction cannot occur by ultrasonic irradiation in water. However, with both ultrasonic effects and the reducing effect of...
EtOH, the reduction can proceed. Therefore, the reduction of Au$_2$O$_3$ hydrate and Ag$_2$O is attributed to ultrasound cavitation and the reducing effect of EtOH.

The difference between the rates of reduction of Au$_2$O$_3$ hydrate and Ag$_2$O is attributed to the difference in the thermodynamic stability [17], and existence of stronger reducing agent oriented from EtOH. As for thermodynamic stability, theoretically, the decomposition properties of Ag$_2$O (Ag$_2$O → 2Ag $+$ $\frac{1}{2}$O$_2$, $\Delta G = 0$ at 467.8 K) are different from those of Au$_2$O$_3$ (Au$_2$O$_3$ → 2Au $+$ 3/2O$_2$, decomposes at room temperature [18], and $\Delta G = 0$ at 2.7 K, as calculated using HSC Chemistry 5). Au$_2$O$_3$ hydrate is more stable than Au$_2$O$_3$ but more reducible than Ag$_2$O. Thus, Au$_2$O$_3$ hydrate and Au$_2$O$_3$ are more unstable than Ag$_2$O and are easily reduced by the heat of the hot spot. Au$_2$O$_3$ hydrate decomposes at approximately 653 K [11]. As for existence of stronger reducing agent, EtOH was oxidized to acetaldehyde during the reduction of Au$_2$O$_3$ hydrate (3CH$_3$CH$_2$OH $+$ Au$_2$O$_3$ → 3CH$_3$CHO $+$ 3H$_2$O $+$ 2Au) [19]. Au NPs acted as a catalyst for EtOH oxidation. Acetaldehyde has a stronger reducing effect than EtOH and promotes the reduction of Au$_2$O$_3$ hydrate. In the case of Ag, Ag could not catalyze the reaction; thus, acetaldehyde was not generated. Ultrasonic irradiated ethanol produces a reductant by hydroxyl radicals (CH$_3$CH$_2$OH $+$ OH$^-$ $\rightarrow$ CH$_3$CHO$^+$ $+$ H$_2$O). The reduction of Ag$_2$O may be promoted by the reductant (2CH$_3$CHO$^+$ $+$ Ag$_2$O $\rightarrow$ 2Ag $+$ 2CH$_3$CHO $+$ H$_2$O) [8].

Ag$_2$O irradiated for 120 min showed peaks attributed to Ag alkoxide.

The peaks were not observed in Ag$_2$O irradiated for 180 min. It is reported that irradiation of ethanol produce ethoxy radical and hydroxethyl radical (CH$_3$CH$_2$OH $+$ OH$^-$ $\rightarrow$ CH$_3$CHO$^+$ $+$ H$_2$O [20]) (CH$_3$C$^+$HOH $+$ CH$_3$CH$_2$OH $\rightarrow$ CH$_3$CH$_2$O$^+$ $+$ CH$_3$CH$_2$OH [21]). Based on the report, it is possible that Ag alkoxide is produced by the reaction of Ag$^+$ with ethoxy radicals produced by ultrasonic irradiation of ethanol. However, Ag alkoxide is very unstable, the formation and decomposition of Ag alkoxide are repeated. Therefore, the Ag alkoxide was measured accidentally in 120 min.

The Au$_2$O$_3$ hydrate changed from dark red to gold, and Ag$_2$O changed from blackish gray to silvery white, indicating the occurrence of reduction reactions.

### 3.2.2. Particle growth by ultrasonic irradiation

Fig. 5 shows the SEM images of Au$_2$O$_3$ hydrate powder and Ag$_2$O powder after ultrasonic irradiation. The peaks were not observed in Ag$_2$O irradiated for 180 min. It is reported that irradiation of ethanol produce ethoxy radical and hydroxethyl radical (CH$_3$CH$_2$OH $+$ OH$^-$ $\rightarrow$ CH$_3$CHO$^+$ $+$ H$_2$O [20]) (CH$_3$C$^+$HOH $+$ CH$_3$CH$_2$OH $\rightarrow$ CH$_3$CH$_2$O$^+$ $+$ CH$_3$CH$_2$OH [21]). Based on the report, it is possible that Ag alkoxide is produced by the reaction of Ag$^+$ with ethoxy radicals produced by ultrasonic irradiation of ethanol. However, Ag alkoxide is very unstable, the formation and decomposition of Ag alkoxide are repeated. Therefore, the Ag alkoxide was measured accidentally in 120 min.

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and low melting points. Thus, sintering and pounding of AuNPs proceed faster than those of bulk Au using all ultrasonic energy since there is no further reduction. Therefore, AuNPs repeatedly collide and easily grow due to the localized high temperature and microjet during bubble collapse [22,23].

In the case of Ag, the particles became slightly smaller. The difference in particle growth compared to that of Au is attributed to the difference in the ease of reduction and surface free energy [24]. The mechanism is as follows. First, Ag$_2$O was slowly decomposed, and AgNPs were deposited on the Ag$_2$O surface. Ag$_2$O is less reducible than Au$_2$O$_3$ hydrate; thus, more ultrasonic energy is required to reduce Ag$_2$O than Au$_2$O$_3$ hydrate. Therefore, not enough energy to produce much NPs left. Second, the attached AgNPs grew on the Ag$_2$O surface, and the remaining Ag$_2$O was reduced upon ultrasonic irradiation. The reduced Ag$_2$O lost oxygen; thus, its size was reduced because particle volume is decreased by metalization. Furthermore, Ag was not easily agglomerated because Ag$_2$O was reduced slowly, and AgNPs were deposited on the Ag$_2$O surface, making Ag less likely to collide with each other. Besides, the possibility of Ag agglomeration was low owing to the low surface free energy of Ag. In summary, the use of ultrasound energy to decompose and grow Ag, the difficulty in reducing Ag$_2$O, and the poor Ag agglomeration affected the size of Ag particles generated after 180 min of irradiation. Fig. 6 shows the difference between the mechanisms of Au and Ag particle growth.

Fig. 5. Scanning electron microscopy (SEM) images of (A) Au$_2$O$_3$ hydrate and (B) Ag$_2$O.
3.3. Ultrasonic irradiation of a mixed powder of Au$_2$O$_3$ hydrate and Ag$_2$O

3.3.1. Reduction by ultrasonic irradiation

Fig. 7 shows the XRD patterns of the mixed powders of Au$_2$O$_3$ hydrate and Ag$_2$O with different molar ratios (Au:Ag) of (a) 1:3, (b) 1:1, and (c) 3:1 after ultrasonic irradiation. The faster reduction of Ag$_2$O in the composite powders is attributed to the strong reducing effect and high activity of AuNPs obtained via the reduction of Au$_2$O$_3$ hydrate. EtOH was oxidized to acetaldehyde, which promoted the reduction of Ag$_2$O. In addition, the generated Au particles were highly active and acted as catalysts for Ag$_2$O reduction [25].
3.3.2. XRF of irradiated mixed powder

Fig. 8 shows the XRF compositional analysis of the irradiated mixed powder. There is a slight difference compared to starting materials, but in this study, the Fundamental Parameter method was used. The inclusion of light elements, such as oxygen, adversely affected the measurement accuracy. In addition, the synthesized Au–Ag alloy is a powder with a very rough surface with a size of a few microns, so the surface X-ray fluorescence absorption fluctuated during the measurement, and the solid solution alloy is not perfect and varied in composition from place to place. Therefore, the measured compositional ratio was almost the same as that of the starting powders.

3.3.3. Refinement of lattice constants

Table 1 and Fig. 9 show the refined lattice constants of Au, Ag, and mixed powders after ultrasonic irradiation. The deviation from the theoretical value in Fig. 9 may be due to the possibility that the composition is not completely homogeneous, hydrates is included, or there is an error in the weighing process. The refined lattice constants of Au and Ag were 0.407714 and 0.408591 nm, respectively, which are comparable to the theoretical values (JCPDS cards are 03-065-2871 for Ag and 00-004-0784 for Au). The lattice constants of the mixed powders were between those of Au and Ag, indicating that an all proportional solid solution of Au and Ag was formed. Furthermore, the lattice constants of the sample irradiated for 120 min has small deviations from theoretical values than those of the sample irradiated for 10 min, indicating that ultrasonic cause intense pounding and composition became homogeneous. Therefore, ultrasonic irradiation promoted alloying in Au–Ag all proportional solid solution system.

3.3.4. SEM and EDX analyses of the irradiated mixed powders

Fig. 10 shows the SEM images of the irradiated mixed powders. The particles grew with an increase in the irradiation time. Fig. 11 shows the EDX images of the powders. Au and Ag were separately complexed in the sample with a short irradiation time, whereas Au and Ag were mixed and alloyed in the sample with a long irradiation time. Based on this result, the alloying mechanism is as follows. First, the reduction of \( \text{Au}_2\text{O}_3 \) hydrate, which is relatively easy, proceeded, and Au clusters and acetaldehyde were produced instantly upon ultrasonic irradiation. The obtained Au clusters were attached to the \( \text{Ag}_2\text{O} \) surface. Second, acetaldehyde, which is a strong reducing agent, and the attached Au clusters, which are catalysts, promoted the reduction of \( \text{Ag}_2\text{O} \); thus, it occurred in just 10 min. Third, with the hot spots and high pressure resulting from ultrasonic irradiation, the reduced Ag was transformed to AgNPs due to the fast reduction and formed an alloy core with Au clusters. Smaller Au and Ag particles easily form an alloy [26], and nanoparticles easily diffuse and form alloys. Nanoparticles are reported to have a lower melting point [27, 28]. The lower melting point means that the particles diffuse more rapidly. Intense diffusion by nanoparticulation and intense pounding by ultrasound are the driving forces of alloying. Finally, the alloy core was agglomerated and compounded because of the repeated collision with other NPs owing to ultrasonic shock waves and microjet. At the same time, the ductility and ductility of Au promoted the alloying process. This reaction mechanism was fast because of the ultrasonic effects, as shown in Fig. 12. Therefore, ultrasound enhances the diffusion and alloying of Au and Ag and cause the avalanche reactions. This process is termed sonochemical alloying.

3.3.5. Melting point analysis of the irradiated mixed powder

Table 2 and Fig. 13 show the melting points of the mixed powders of \( \text{Au}_2\text{O}_3 \) hydrate and \( \text{Ag}_2\text{O} \). The melting points of Au and Ag were 1316.2 K and 1209.2 K, respectively, which are almost the same as the theoretical values [28, 29]. The melting points of the mixed powders were
between that of Au and Ag and varied with the composition, indicating that Au–Ag alloys were formed via sonochemical alloying. Composites with core–shell structures have been obtained via conventional ultrasonic irradiation [25], but in this study, the alloys were achieved at lower temperatures. In the conventional method, in which composite particles are loaded onto a substrate, reduction of gold and silver does not occur simultaneously [25]. However, in this study, high temperature, shock waves, and microjets resulting from ultrasonic irradiation promoted simultaneous redox reactions, and alloys were obtained.
4. Conclusions

In this study, we investigated the reduction of irradiated noble-metal oxides in EtOH and the effect of ultrasonic irradiation on noble-metal mixed powders. In the former, both $\text{Au}_2\text{O}_3$ hydrate and $\text{Ag}_2\text{O}$ were reduced at room temperature and atmospheric pressure, and the reduction rate varied with the thermodynamic stability of the oxides. Furthermore, the growth of Au and Ag particles was different. Au particles were obtained in a shorter time and were larger. In the latter, the reduction of $\text{Ag}_2\text{O}$ in the mixed powders of $\text{Au}_2\text{O}_3$ hydrate and $\text{Ag}_2\text{O}$ was faster than that of $\text{Ag}_2\text{O}$ alone. Au particles acted as a catalyst. Furthermore, an Au–Ag all proportional solid solution was obtained at 313 K within 10 min of ultrasonic irradiation of the mixed powder in EtOH. This sonochemical alloying method can form alloys at low temperatures in a short time; thus, it is a promising method for alloying.

CRediT authorship contribution statement

Yamato Hayashi: Conceptualization, Methodology, Investigation, Funding acquisition, Writing – review & editing, Project administration. Yusuke Ebato: Writing – original draft, Formal analysis. Ryoma Onishi: Formal analysis. Hirotsugu Takizawa: Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Table 2
Melting point of Au/Ag alloy after ultrasonic irradiation.

| Molar ratio (Ag/Au) | 10 min Irradiation | 120 min irradiation |
|--------------------|--------------------|---------------------|
| 1/0                | 1209.2             |                     |
| 3/1                | 1258.1             | 1260.2              |
| 1/1                | 1286.5             | 1288.8              |
| 1/3                | 1307.2             | 1309.6              |
| 0/1                | 1316.2             |                     |

Fig. 12. Alloying mechanism of the mixed powders under ultrasonic irradiation.

Fig. 13. Melting points of Au–Ag alloys with different molar ratios after ultrasonic irradiation. (Blue line: 10 min irradiation, Red line: 120 min irradiation).
