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Preparation of porous silver particles using ammonium formate and its formation mechanism

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ABSTRACT

Here we report the preparation of two different types of macroporous silver particles (round and coral) by simple chemical reduction using ammonium formate. We also discuss the chemical mechanism of silver particle and macroporous silver particle formation. The synthesized round type and coral-type porous silver particles were 20–50 μm and 30–150 μm in size and their pores were 100–200 nm and 1–2 μm across, respectively. They were characterized by particle distribution analysis, X-ray diffraction, and scanning electron microscopy.

1. Introduction

Silver powder is an important material in the electronics industry because of its high electric conductivity and chemical stability. Macroporous silver powder, in particular, has important applications in catalysis and in the manufacture of secondary batteries, fuel cells, and chemical sensors, which require high surface-to-volume ratios [1,2].

Several methods have been used for porous silver. Dome-shaped porous silver was fabricated by Jin and Yuan using a colloidal templating method [3]. This method involves filling the spaces between a close-packed array of monodisperse spheres with poly(ethyleneimine) hydrogels and silver ions to form a solid skeleton around the spheres, and subsequently removing the colloidal crystalline template by calcination or solvent extraction. Cellulose fiber has also been used as a template with silver nanoparticles for the production of porous silver nanostructures [4], and silica hydrogel has been used to fabricate porous silver monoliths in a one-pot reaction [5]. A combination of Triton X-114 with Ludox silica sol and dextran can also be used to prepare porous silver monoliths [6].

Aside from these methods, a simple chemical reduction method, which would not necessitate any additional treatment and template technique, can also be considered for the production of porous silver because the chemical reduction method has the ability to produce silver powders of various shapes by the use of different reducing agents [7–10].

Formic acid (or formate), one of the well known reducing agent for Ag powders, has an ability of one step reduction and low reactivity with silver ion so that it has been popularly used for controlling the morphology and particle size of Ag with proper additives [11,12]. In addition, recently, porous silver was prepared from simple chemical reduction using the ionic liquid N-(2-hydroxyethyl)ammonium formate [13]. In this method, in order to prepare porous silver monolith with 200 nm pores, a microwave reaction vessel filled with $AgNO_3$ and ammonium formate was used to keep pressure and temperature during the reaction.

In the present work, we described a chemical reduction method using ammonium formate for two different type macroporous silver particles in standard condition for temperature and pressure, and the formation mechanism of Ag particles and porous structure is discussed.

2. Experimental

2.1. Preparation of Ag particles

The preparation of macroporous Ag particles and Ag particles using NH_4COOH reduction is illustrated in Fig. 1. $AgNO_3$ (>99% purity) was dissolved in distilled water at room temperature, and then NH_4COOH solution was added to induce reduction. The mixed solution was stirred at room temperature for 5 min. A dark brown precipitate was formed during the stirring and it was maintained in the solution for different durations. The product was washed five times with distilled water and then dried at 50 °C for 12 h.

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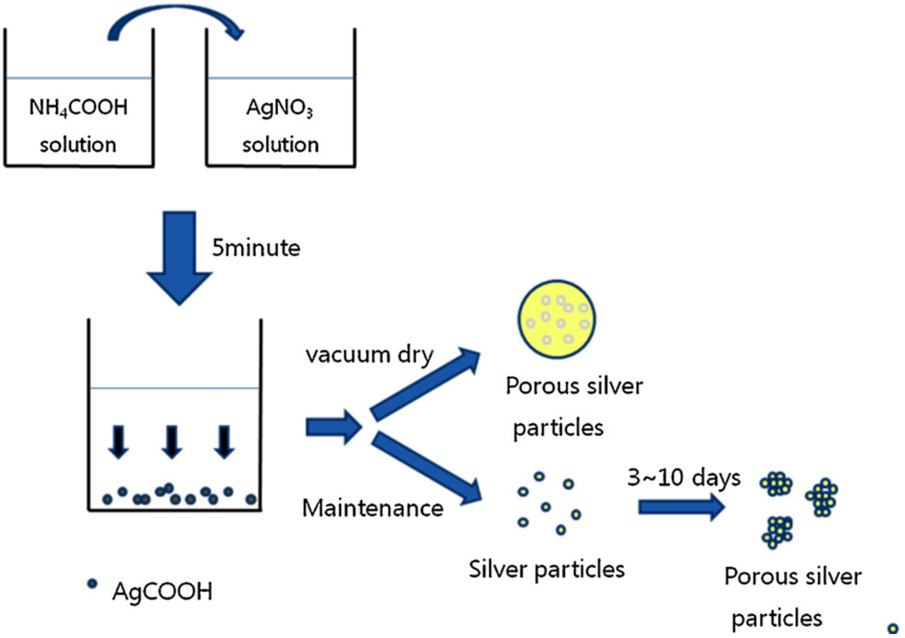

Fig. 1. Schematic of the ammonium formate reduction synthesis of porous silver particles and silver particles.

2.2. Preparation of macroporous Ag particles

The two types of macroporous Ag particles (round type and corral-type) are prepared in different ways. For the round type particles, the dark brown precipitate was washed several times and then dried under vacuum for 12 h. For the coral-type particles, the solution prepared from $AgNO_3$ and NH_4COOH, which contains reduced Ag particles, was maintained for different durations to allow the connecting reaction between Ag particles to occur. The product was washed five times with distilled water and then dried at 60 °C for 12 h.

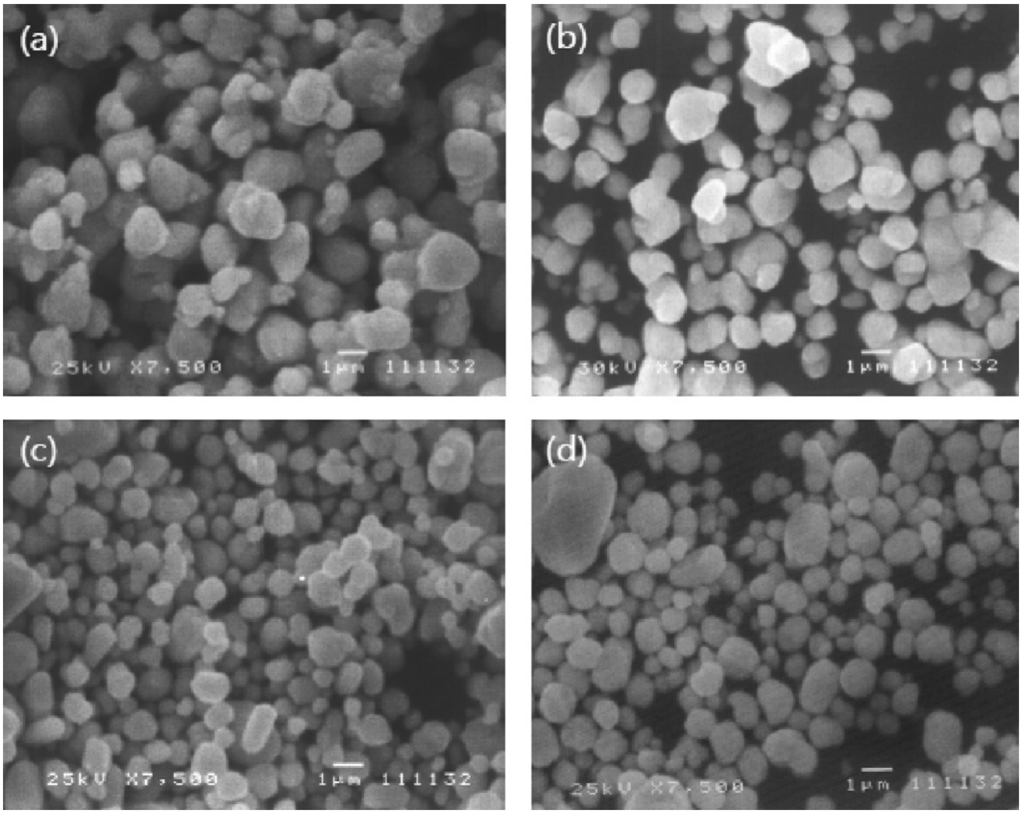

Fig. 2. SEM image of silver powder from different concentration of ammonium formate and silver nitrate. (a) 0.1 M NH_4COOH, (b) 0.5 M NH_4COOH, (c) 1.0 M NH_4COOH, and (d) 3.0 M NH_4COOH.

2.3. Characterization of macroporous Ag particles

The final products were characterized using an X-ray diffractometer (Siemens German, D-5000), a surface area analyzer (Micromeritics U.S.A., ASAP 2010), and a scanning electron microscope (FESEM; JEOL Japan, JSM 6330F).

3. Results and discussion

3.1. Formation of Ag particles

We first measured the influence of the $AgNO_3$ and NH_4COOH concentrations, which have a major influence on the morphology and particle size of the final product.

In contrast to hydrazine and hydroquinone, which are popular reducing agents for Ag powders [14,15], NH_4COOH exhibited considerably low reactivity, and allowed facile control over the morphology and particle size. Fig. 2 shows the particle sizes and morphologies of Ag powders prepared using different NH_4COOH concentrations and 1.0 M $AgNO_3$. Clearly, the particles range in size from 1 μm to 2 μm, and all have a spherical morphology. However, we find a different reaction speed in each experiment. Fig. 3 shows the average time taken to form the intermediate product and Ag as a function of the NH_4COOH concentrations. When NH_4COOH reacts with $AgNO_3$, a brown intermediate product is formed within a few minutes ($\leq$12 min), which then transforms into Ag. Both the reaction time for forming the intermediate product and its subsequent transformation into Ag particles increases with the NH_4COOH concentration. These results can be explained by two different reaction routes that are related to the catalytic effect of silver ion, and which are discussed and explained in detail below.

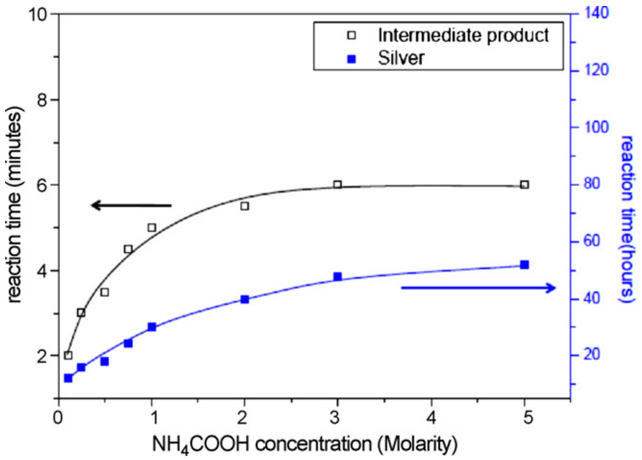

Fig. 3. Reaction speed change from different ammonium formate concentration.

Because of the slow reaction speed of NH_4COOH, it was possible to collect samples from each step in the formation of Ag particles. Fig. 4 shows the Ag particles at different points in the formation process, starting from the large reactant particles. The powders prepared from 1.0 M $AgNO_3$ and 1.0 M NH_4COOH were collected at different reaction times. Fig. 4(a) shows the initial stage of the reaction: only large round-shaped intermediate reactant particles 20–50 μm in size are seen, showing that Ag particles had not yet begun to form. Next, small Ag particles are formed on the reactant surface as reduction begins (Fig. 4(b)), and these small particles are subsequently separated from the reactants (Fig. 4(c)). Finally, the large round-shaped reactant particles disappear, and only round-shaped Ag particles remain (Fig. 4(d)).

It was possible to observe this reaction process only because of the uniquely slow reduction speed of NH_4COOH. Generally, when Ag^+ come into contact with substances containing ammonium ions,

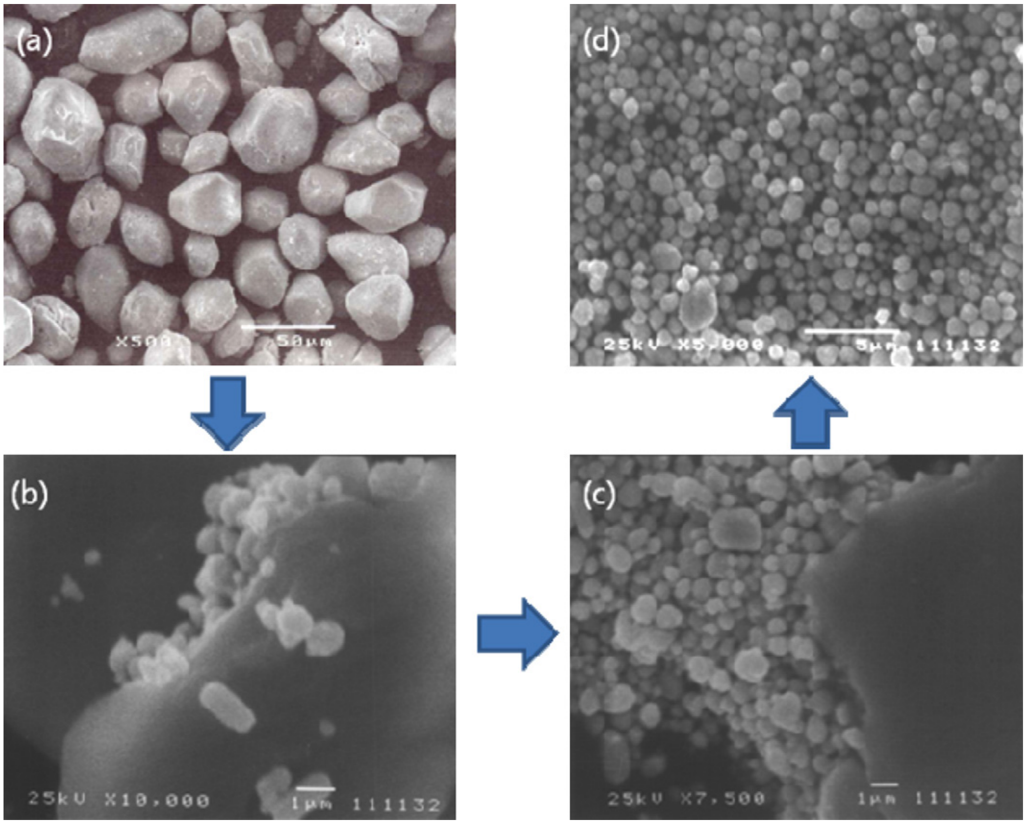

Fig. 4. The formation process of silver particles; collected from different reaction time: (a) 5 min, (b) 10 h, (c) 20 h, and (d) 30 h.

Tollen's reagent ($Ag(NH_3)_2^+$) is formed. To make Ag powder, this reagent is usually reduced with conventional reducing agents such as hydroquinone and hydrazine. However, the mechanism of the formation process discussed above, which starts from large reactant particles, is different from the mechanism of conventional Tollen's reagent formation. A possible mechanism is that silver formate forms as an intermediate product [16]. The proposed reaction is

$$AgNO_3 + NH_4COOH \rightarrow AgOOCH + NH_4^+ + NO_3^- \quad (1)$$

$$AgOOCH \rightarrow Ag + 0.5CO_2 + 0.5HOOCH\,(25\,^\circ C) \quad (2)$$

First, the reaction forms silver formate from Ag^+ and $COOH^-$. However, silver formate is stable in aqueous media only below 5 °C; at room temperature, it slowly decomposes into Ag, CO_2, and HOOCH.

To verify this proposed reaction mechanism, we performed XRD analysis of the products from each formation step corresponding to Fig. 4 and mass spectroscopy on gas released during the reaction. Indeed, the silver formate XRD peak is present in the XRD spectrum (see Fig. 5) and mass spectroscopy identified the released gas as CO_2.

However, when the ammonium concentration is lower than stoichiometric point of $AgNO_3$, the reaction does not follow the same route:

$$AgNO_3 + 0.5NH_4COOH \rightarrow 0.5AgOOCH + 0.25Ag(NH_3)_2^+ + NO_3^- + 0.25Ag^+ + 0.5H^+ \quad (3)$$

$$0.5AgOOCH \rightarrow 0.5Ag + 0.25HCOOH + 0.25CO_2\,(25\,^\circ C) \quad (4)$$

$$0.25Ag^+ + 0.25HCOOH \rightarrow 0.25AgCOOH + 0.25H^+ \quad (5)$$

$$0.25AgOOCH \rightarrow 0.25Ag + 0.125HCOOH + 0.125CO_2\,(25\,^\circ C) \quad (6)$$

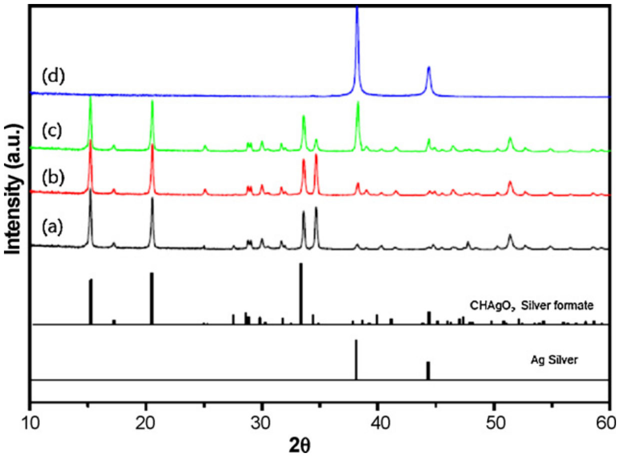

Fig. 5. XRD data of products collected from different reaction time: (a) 5 min, (b) 10 h, (c) 20 h, and (d) 30 h.

Low concentrations of NH_4COOH leads to the formation of Tollen's reagent because of insufficient $COOH^-$. Once Tollen's reagent is formed, it does not react with $COOH^-$ because this reagent is stable. Hence, the remaining Ag^+, resulting from the decomposition of silver formate, reacts instead with the $COOH^-$ to form silver formate. In addition, this reaction route is faster than the reaction route that does not produce Tollen's reactant and Ag^+. The reason for this is the catalytic behavior of the unreacted Ag^+ in reaction (3) [17,18]. By changing its ionic valence and exchanging electrons with silver formate, the remaining Ag^+ facilitates the decomposition of silver formate until Ag^+ forms silver formate.

$$AgOOH \xrightarrow{Ag^+, Ag^{++}, Ag^{+++}} 0.5Ag + 0.25HCOOH + 0.5CO_2 \;(25\,^\circ C) \quad (7)$$

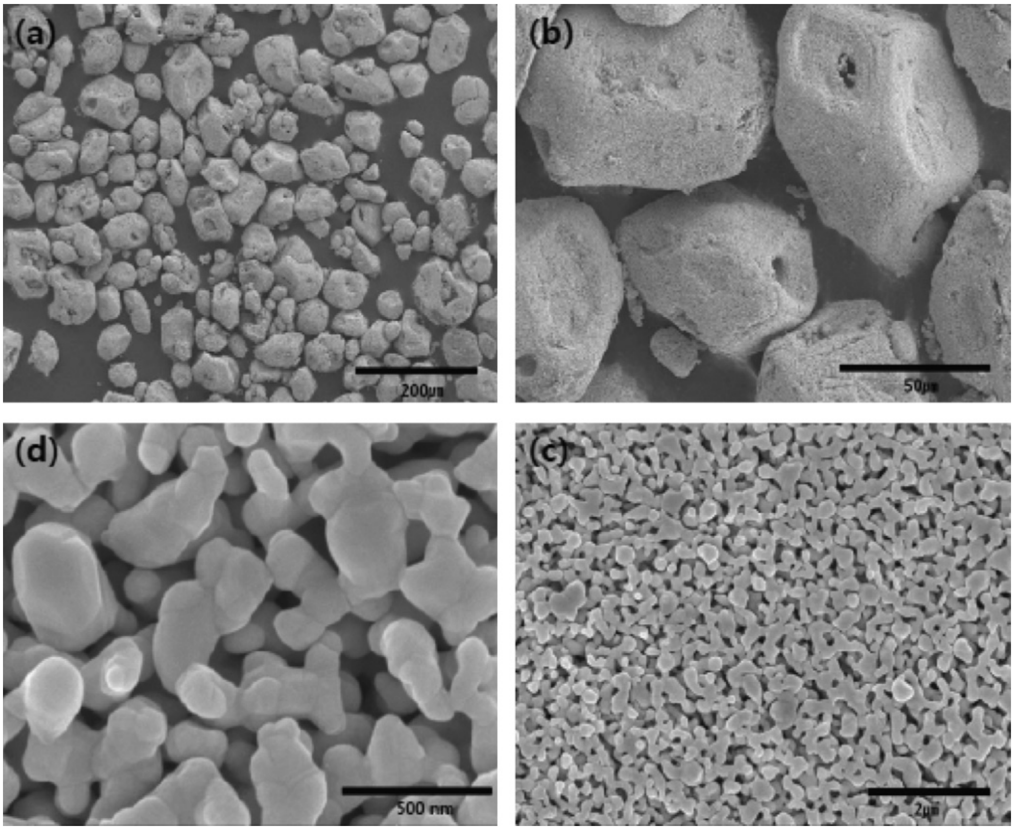

Fig. 6. SEM images of round type porous silver particles: (a) 100×, (b) 500×, (c) 10,000×, and (d) 50,000×.

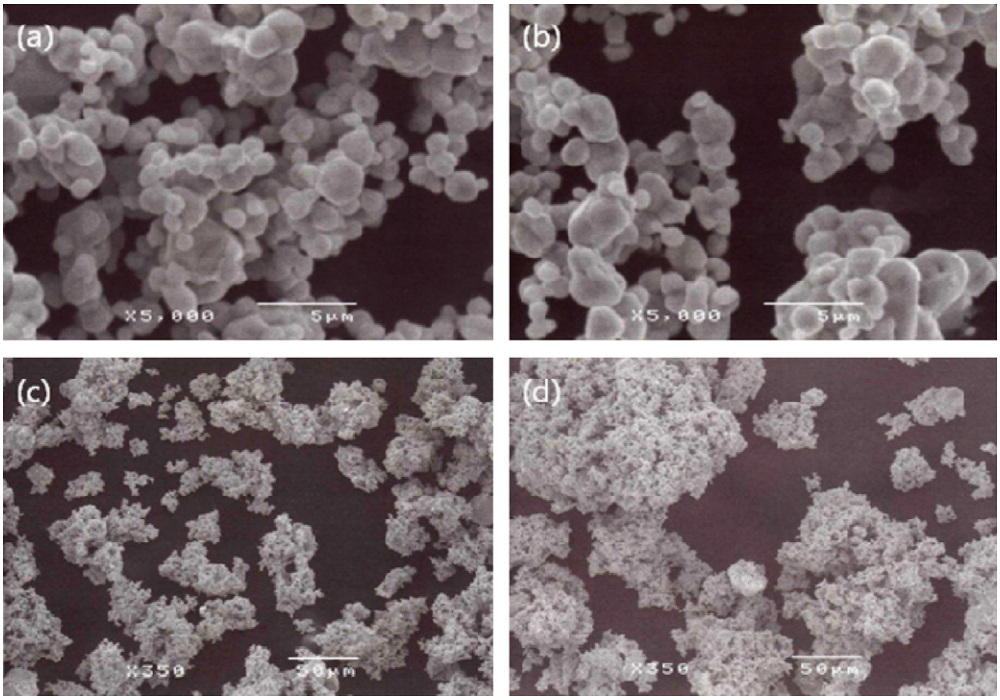

Fig. 7. SEM image of silver powders with different keeping time at room temperature ($0.5AgNO_3 + 2.0HCOONH_4$): (a) 3 days, (b) 5 days, (c) 8 days, and (d) 10 days.

To demonstrate the suggested reaction (7), precipitated silver formate was washed four times and mixed into both the distilled water and the solution in which only $AgNO_3$ was dissolved. Silver formate in the $AgNO_3$ solution decomposed and Ag particles were obtained, but the initial silver formate in the distilled water did not change at all.

4. Formation of macroporous Ag particles

Two different types of macroporous Ag particles (the round type and the coral-type) were synthesized according to the two synthesizing processes that will be discussed. Fig. 6 shows SEM images of round type porous Ag particles. The macroporous par-

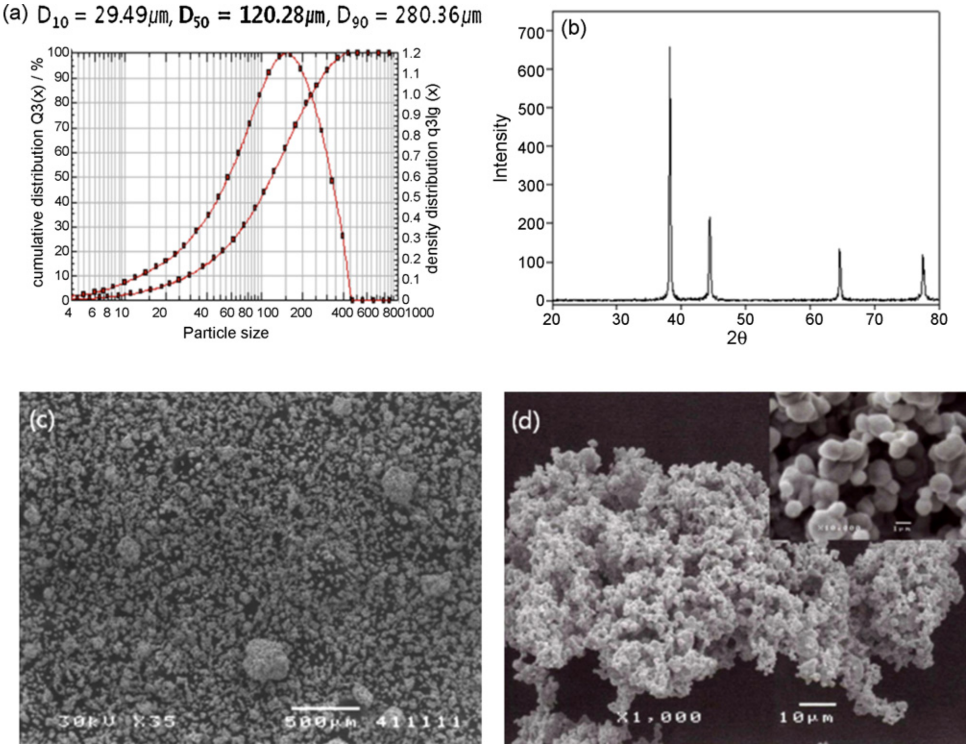

Fig. 8. (a) Particle distribution, (b) XRD peak, (c) SEM image (35×), and (d) SEM image (1000×) of porous silver synthesized from $AgNO_3 + HCOONH_4$.

ticles are from direct vacuum drying of silver formate powder at 60 °C for 12 h. It is apparent that each porous particle maintains the size and shape of the silver formate particles, which were precipitated from $AgNO_3$ and NH_4COOH. In addition, their macroporous structure consists of 100–300-nm particles with 100–200-nm cavities. In order to understand porous structure of synthesized Ag particles, BET analysis was conducted using N_2 gas at 77 K. The determined specific surface area was 2.89 m^2/g and measured adsorption average pore diameter was 200.721 nm. The formation of this macroporous structure can be explained by the gas released by the decomposition of silver formate. In contrast with decomposition in solution, under vacuum silver formate decomposes to Ag, CO_2, and H_2, and it is this release of gas that makes cavities in the particles.

$$2AgOOCH \rightarrow Ag + 2CO_2 + H_2 \quad (8)$$

Compared with the round type Ag particles, preparation of the coral-type macroporous Ag particles requires more time to synthesize because the connecting reaction between small Ag particles is slow. After the individual small Ag particles are formed, the reaction between them begins when they are put into a solution of Ag and formic acid. Fig. 7 shows SEM images of Ag powders maintained for different durations in a solution containing 1.0 M $AgNO_3$ and 2.0 M NH_4COOH at room temperature. As seen, dispersed particles begin by forming clusters and eventually form porous particles with the passage of time. The formation of porous particles was remarkably accelerated when the solution was maintained for more than 8 days, and most clustered particles had dimensions of 100 μm through 10 days in solution. Beyond 10 days, there was no size increase, suggesting that the agglomeration and disintegration of porous particles occurs simultaneously during aging due to interactions between small particles created after reduction.

The mechanism connecting Ag particles is not clear, but we hypothesize that the connecting reaction is caused by a surface interaction between Ag particles and formic acid. Ag particles are well known as a catalyst for formic acid decomposition [19]. Instant electron exchange between the Ag surface and formic acid induces the decomposition, and the Ag surface is left in an unstable state. To offset this unstable surface, Ag particles join together. To check our hypothesis, Ag powder with 1 μm particle size and good dispersion was maintained in a solution of formic acid for 7 days. After 7 days, the Ag particles are connected with each other, forming clusters.

Fig. 8 shows SEM images (and the particle size distribution) of coral-type porous Ag powder formed under the conditions optimum to maximize the particle size. The porous structure is well organized and the mean particle size is 120 μm. In addition, Fig. 8(b) shows that the XRD spectrum of the final product displays a clean Ag peak.

5. Conclusion

Round type and coral-type porous Ag powders were synthesized by simple chemical reduction using NH_4COOH. The reaction between $AgNO_3$ and NH_4COOH first formed 20–50-μm silver formate particles (intermediate), which decompose into Ag particles. Increasing the Ag^+ concentration accelerates the silver formate decomposition rate. Round type macroporous Ag particles, consisting of 100–300-nm particles with 100–200-nm cavities, were fabricated by vacuum drying of silver formate. A connecting reaction between Ag particles was generated by maintaining the solution containing Ag particles and formic acid. The maximum particle size for the coral-type porous Ag is 120.28 μm (D50), and its average pore size is 1–2 μm.

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