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Counter-ion effects of silver salt on the production yield of silver nanoparticles in alcohol reduction process

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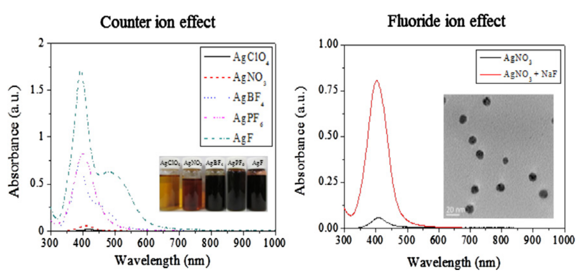
HIGHLIGHTS

- Silver nanoparticles were prepared with silver salts of various counter-ions via alcohol reduction process.
- Reduction degree of silver ions was very much dependent on the kinds of counter-ions.
- Inorganic silver salts containing fluoride (AgF, $AgPF_6$, and $AgBF_4$) showed a high reduction yield.

GRAPHICAL ABSTRACT



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ABSTRACT

In the fabrication of silver nanoparticles, the reduction of silver ions is an essential step. In the large-scale synthesis of silver nanoparticles for industrial applications, there are limitations such as economic aspect and side effect of unreduced silver ions. To develop the practical fabrication methods, various fundamental studies for the reduction of silver ions have been reported. In this study, the effect of counter-ions on the reduction yield in alcohol reduction process was investigated. $AgClO_4$, $AgNO_3$, $AgBF_4$, $AgPF_6$, and AgF were employed as silver precursors. The UV–vis spectrum and ISE data show that reduction yield strongly depends on the counter-ions and has the following order: AgF > $AgPF_6$ > $AgBF_4$ > > $AgNO_3$ > $AgClO_4$. This result was explained based on the role of fluoride ions during the reduction process of silver ions. The reduction yield was increased as the amount of fluoride ions was increased due to the released free $[H^+]$.

1. Introduction

Silver nanoparticles fabricated by the reduction of silver ions have been used as a material for olefin separation membrane [1], antibiotic [2], sensoring device [3], and electronics [4] due to their antibacterial [5,6], electronic [7], and optical [8,9] properties. However, large-scale synthesis of the silver nanoparticles still remains as a challenge. Especially, the reduction yield is a major issue because the reduction yield is directly related with economic efficiency. Since the silver is an expensive noble metal, the higher production yield of silver metal particles by the reduction of silver ions would be important in the application of silver nanoparticles. For example, remaining silver ions during the process caused the cost loss itself; requiring the separation processes due to the side effect of silver ions which triggered poor stability in olefin membrane performance [10]. Therefore, the study for the optimization of the reduction yield is essential.

In this paper, the reduction yield depending on the silver salt was investigated. Usually counter is considered as a "spectator ion" because of the thought that this does not participate in the reduction, so that counter ion has been omitted in the elucidation of reduction mechanism [11,12]. In spite of this fact, various silver salts affect the reduction yield in synthetic processes, providing an opportunity to maximize the reduction yield through various silver

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salts. Kim et al. tried to explain this phenomenon with interaction of silver cations with polymer [13].

Since the alcohol reduction process is known as a chemical reducing agent free method, the effect of counter-ion in alcohol reduction process has been widely examined. In this process, alcohol acts both as a solvent of the silver precursor and as a reducing agent, and silver ions are mainly reduced by redox reaction between the silver precursor and the solvent [14,15]. The several silver precursors which are inorganic silver salt and soluble in ethanol at the reaction condition were selected. Polyvinylpyrrolidone (PVP) was employed to stabilize the surface energy of nanoparticle. PVPs can be adsorbed at the particle surface and their polymer chains prevent the particle aggregations [16]. The nanoparticles synthesized by this process were analyzed in the aspect of the reduction yield and particle size. The role of counter-ion was demonstrated by varying the amount of counter-ions and adding other salts.

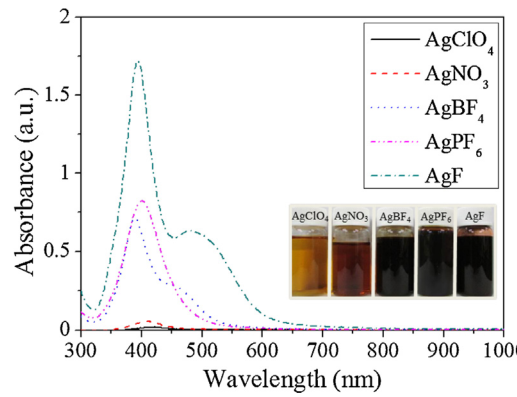

Fig. 1. UV–vis spectra of silver colloids and their photographs prepared using different silver salts; $AgClO_4$, $AgNO_3$, $AgBF_4$, $AgPF_6$ and AgF.

2. Experimental

All silver salts, including silver perchlorate ($AgClO_4$ < 99.99%), silver nitrate ($AgNO_3$ < 99.99%), silver tetrafluoroborate ($AgBF_4$ < 99.99%), silver hexafluorophosphate ($AgPF_6$ < 99.99%), and silver (I) fluoride (AgF < 99.99%) were purchased from Alfa Aeser. Poly(vinyl pyrrolidone) (MW = 10,000) was purchased from Sigma Aldrich. Ethanol (99.9%) was purchased from Daejung Chemicals and Metals Company. All chemicals were used without further purification.

Silver salt solution was prepared by dissolving 0.004 mol of silver ion in 50 ml of ethanol. Also, PVP solution was prepared by dissolving 0.5 g of PVP in 50 ml of ethanol. Based on the fact that Ag^+ is adsorbed on the carbonyl group in the PVP [17], the amount of silver salt added was determined to be [C = O in PVP]:[Ag] = 1:1. Both solutions were mixed together and refluxed at 80 °C for 4 h with magnetic stirring.

For the reduction yield analysis, UV–vis spectrophotometer (Agilent Technologies, Agilent 8435) and ion selective electrode (ISE; Thermo Scientific Orion, Orion 96-16 Silver/Sulfide combination electrode) were used. In case of using UV–vis spectrophotometer, samples were diluted with ethanol by adding 0.01 ml of each colloid to 3 ml of ethanol. ISE samples were diluted by adding 1 ml of prepared colloid to 9 ml of distilled water, because ISE is designed to use in the aqueous medium. The size and morphology of silver particles were assessed by transmission electron microscopy (TEM; JEOL Co., JEM-2100F). For TEM analysis, a drop of colloidal solution was placed on the TEM grid and dried in a drying oven at 40 °C for 24 h.

3. Results and discussion

3.1. Characterization of silver nanoparticles

Fig. 1 shows the UV–vis spectra of silver colloid produced after 4 h reaction and their photograph depending on the silver salt. The color of colloids synthesized from $AgClO_4$, and $AgNO_3$ is transparent yellow. However, other colloids synthesized from $AgBF_4$, $AgPF_6$, and AgF show dark yellow. These differences of color indicate that lots of silver particles interfere the light going through. UV–vis spectrum also shows the same tendency. The maximum UV absorbance of colloid made with $AgNO_3$ and $AgClO_4$ at 405 nm and 422 nm, respectively, was very low comparing with the other Ag colloids. On the other hand, the maximum absorbance of colloid made with $AgBF_4$, $AgPF_6$, and AgF at 389 nm 400 nm 394 nm respectively were over 0.75 (A.U.). Among the many silver salts, AgF showed the highest intensity of the absorbance at 394 nm. It is generally accepted that absorption peak whose maximum peak occurs around 400 nm is related to the formation of silver nanoparticles and its height gives information about the concentration of Ag particles [18,19]. According to this fact, AgF as a silver precursor provide the highest reduction yield for the fabrication of silver nanoparticles. Also, the shoulder peak at 500 nm provides information of aggregates which were formed due to the high particle concentration. It has been reported by El-Sayed and Misra that, as the interparticle distances become smaller than the spherical particle dimension, or even when aggregation occurs, the plasmon resonance red shift, and a second absorption peak at longer wavelength is observed [20,21]. Based on these results, produced particle amount depending on the counter-ion is arranged in the order: AgF > $AgPF_6$ > $AgBF_4$ > > $AgNO_3$ > $AgClO_4$.

Through the ISE measurement, the remaining silver ions in the colloid can be detected. Fig. 2 shows the remaining silver ions in each colloid fabricated by different silver salts. ISE produces the electrical signal when silver ions are adsorbed on the sulfur membrane [22,23]. From this signal it is possible to measure the remaining silver ions in the colloid. Reduction percentage was calculated by comparing the solutions before heating and after heating. As shown in Fig. 2, the colloids using $AgClO_4$ and $AgNO_3$, about 98% of silver ions are remaining that means only 2% of silver ions are reduced into Ag nanoparticles. However, when using $AgBF_4$, the amount of remaining silver ions were reduced to 75%. Also, it was found that 54% of silver ions are remaining when using $AgPF_6$. The smallest amount of remaining silver ions was found when using AgF, which is 11%. When using $AgBF_4$, $AgPF_6$, AgF as a precursor, the reduced amount of silver ion is increased and the highest reduction yield was shown when using AgF. According to this ISE data, the reduction amount is AgF > $AgPF_6$ > $AgBF_4$ > > $AgClO_4$ > $AgNO_3$ which is similar tendency with concentration of synthesized particles detected by UV–vis spectrum.

The TEM images of silver nanoparticles depending on the silver salts showed the size and shape of each particle (Fig. 3). According to these images, it was found that spherical and well-dispersed particles were synthesized and their size was under the 10 nm. However, there are big differences between two groups; one group is using $AgClO_4$ and $AgNO_3$ which shows poor reduction yield in UV–vis spectrum and ISE, and the other group is using $AgBF_4$, $AgPF_6$ and AgF which shows high reduction yield. Although the particles synthesized by using $AgClO_4$ or $AgNO_3$ have ~4 nm core, the particle synthesized by using $AgBF_4$, $AgPF_6$, or AgF have ~8 nm core. Large amount of reduction presumably causes the particle to grow because the source of growing (Ag^0) is increased.

According to the above results, silver inorganic salts containing fluoride showed a good reduction ability. Especially, without reducing agent, AgF is possible to synthesize highly concentrated