

A Study of Particle Size Distribution in NPP process

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ABSTRACT

Noble nanoparticles were fabricated on supporter powder by NPP process, in which nanoparticles were formed on the rotating powder in barrel by using conventional PVD system. The size and distribution of fabricated nanoparticles were observed under various deposition conditions. Glucose and NaCl powders were selected as the supporter powders for the nanoparticle formation and stirring speed of blade was controlled 8 to 30 rpm by DC motor. Particle's size, size distribution and concentration were observed by HR-TEM and ICP-AES and the diameter of Au, Ag, Pd and Pt nanoparticles was 5~15 nm, 5~10 nm, 2~5 nm and 2~3 nm, respectively, by changing mixing condition. As the stirring speed of blade was faster and the weight of filled powder was heavier, average nanoparticle's sizes were smaller. Size uniformity of the particles was fine in faster stirring blade than that in lower speed. These variables were related to exposure time in deposition zone, and shorter exposure time to deposition zone was resulted in fine and well-distributed nanoparticles. The size of Ag on NaCl supporter powder was 10 times compared with Ag on glucose supporter powder induced by difference of surface property of supporter powder. However it was seen by TEM and UV-Vis measurement that the particle size and shape were not changed as increasing concentration.

Keywords: nanoparticles, NPP process, TEM, platinum, size, distribution

1 INTRODUCTION

The nanoscale particles have a high reactivity in a photo or catalytic effects[1-3], show a strong sterilization and deodorant activities in a bacterial membrane with complex surface chemistry and can be more distinctive new quantum dot or hopping site in semiconductor applications[4, 5]. The significant increase in the ratio of surface area to volume with reducing particle size also causes a shift toward blue light[6] with discrete energy band-gap in an optical sensor and a luminescence diode, reduces the difficulties in the transport of medical tracer in a drug delivery system[7], and helps synthesizing new functional materials with a mixture of the nanoscale particles and bulk materials to the super

gigantic magnetic materials and to high electrical or thermal conductivity plastics or glass[8]. There are many methods for manufacturing the nanometer scale particles, which are mechanical grinding process, physical explosion in air or in vacuum, and wet chemical process using oxidation and reduction reagents. Using the above conventional methods, however, it is difficult to make pure and uniformly distributed the nanoscale particles[9] and to fabricate the nanoscale from metal alloys, high melting metals and ceramics. The aggregation of the nanoparticles is happened in a colloidal solution without dispersion agent and toxic chemical agents can be remained in a solution or on the nano particles after the fabrication.

Therefore we invented new nanoparticle fabrication process which was used PVD deposition system to obtain fine and pure nanoparticle. The classic nuclei growth theory was used for fabricating nanoparticles. According to nuclei growth theory, it would be re-evaporated or agglomerated into other nuclei to decrease surface energy when the size of initial nuclei is not larger than r^* (critical radius). However, if the size of nuclei was larger than r^* it was stable and could grow to thin films. In order to prevent the nuclei from developing thin films, it was necessary to stop supplying of vaporized atom before the film formation. This process resulted in obtaining fine nanopartilces, it is called NPP (Nono Particle on Powder). We have manufactured and applied nanoparticles to various field such as chemical catalyst, agriculture, electronic goods etc. In this article, we analyzed particles size and distribution as fabrication conditions in order to obtain nanoparticles of high quality.

2 EXPERIMENTS

Nanoparticels were prepared by NPP method which is explained above. Schematic diagram of NPP system was presented in Figure 1. Fabrication equipment was composed of camber, DC cathode, barrel which had support powder and vacuum systems. Metal particles were deposited on supporter powder by DC sputtering system with 10 cm diameter. Sputtering target was disc type of 0.5 cm (Pt, Pd, Au) or 1.0 cm (Ag) thickness and their purity is 99.99%. The supporter powders such as glucose were stirred by blade in order to hinder films growth of nanoparticles

during depositing. Power density of DC sputtering was $3.0 \sim 6.0 \text{ W/cm}^2$, rotating speed of blade which could be controlled by DC motor was $8 \sim 60 \text{ rpm}$. A concentration of metal nanoparticle in supporter powders was measured by ICP-AES and the size and distribution of nanoparticles were observed by HR-TEM

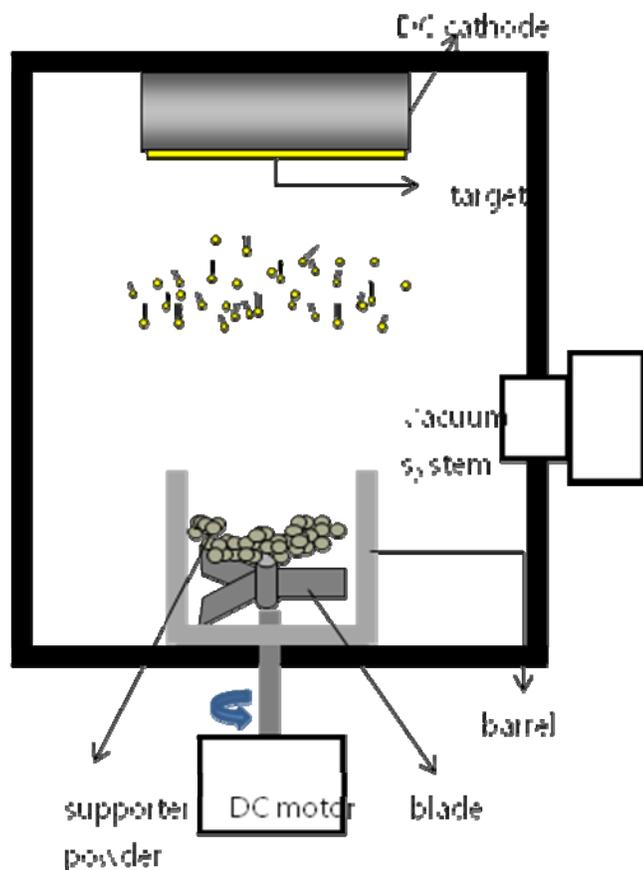


Figure 1 : Schematic diagram of NPP system

3 RESULTS

In order to study influence of rotating speed of blade in barrel on particle size, we fabricated Ag nanoparticles under various stirring speeds. The glucose with $500 \mu\text{m}$ diameter was used as the supporter powder, they were stirred by blade which rotation speed was 8, 15, 30 rpm. Power density on the Ag target was fixed to 3.0 W/cm^2 . The concentration of Ag in glucose powder was about 1,000 ppm by ICP-AES measurement. After making nanoparticles, Ag colloidal solution was synthesized as adding distilled water to Ag nanoparticles for TEM analysis. Figure 2 showed TEM image of Ag nanoparticles when stirring speed is 8 (Figure 2 (a)), 15 (Figure 2 (b)), 30 rpm (Figure 2 (c)). It could be seen that the size of particle at 30 rpm was smaller than at 8 rpm. The distribution of particles was uniform in 30 rpm, too. These results were related with exposing time of supporter powder to deposition zone. When the speed of rotation was fast, the particles could not grow to large particle because deposition time was too short.

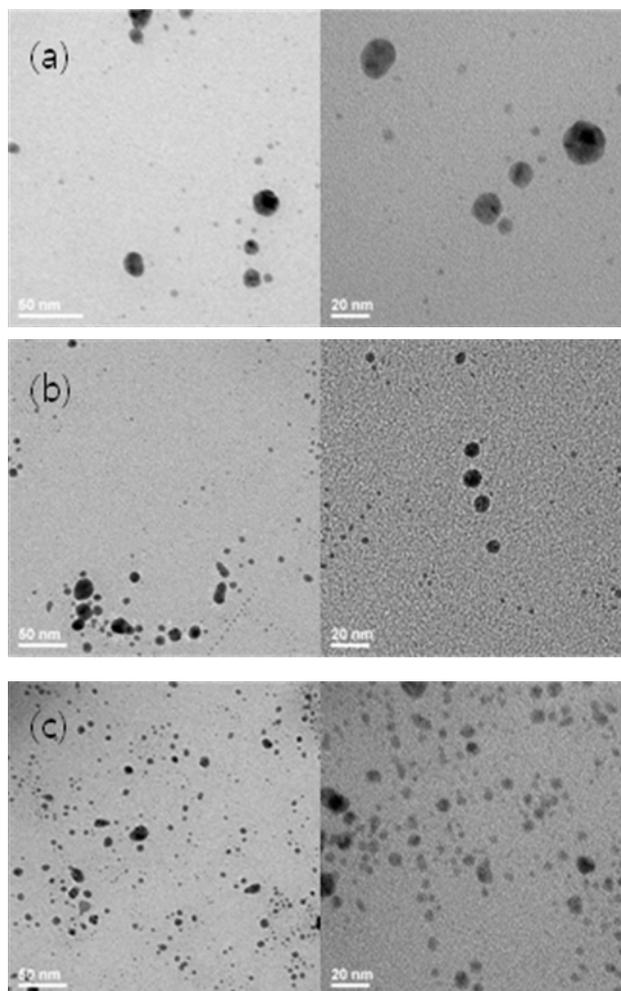


Figure 2 : TEM image of Ag particles which were fabricated under 8 rpm (a), 15 rpm (b) and 30 rpm stirring speed of blade

The size distribution, average size and standard deviation were presented in Figure 3 as a function of the stirring speed. While the fraction of coarsening particles with larger than 15 nm was over 10% in 8 rpm, that was under 1% in 30 rpm. It could be said that the fine and well-distributed particles were obtained at high stirring speed from Figure 3.

Secondly we analyzed influence of supporter powder as using NaCl powder. Ag nanoparticles were made on NaCl supporter powder under 30 rpm, then TEM analysis was carried out and presented in Figure 4. Other deposition conditions were same to above mentioned Ag on glucose. As seen in Figure 4, we could see that the size of Ag was $50 \sim 100 \text{ nm}$. That of Ag on NaCl was 10 times compared with Ag on glucose. It would be guessed that the size difference of Ag particles between glucose and NaCl support powder resulted in surface property of glucose and NaCl. Since heterogeneous nucleation site in NaCl surface was less than in glucose surface and surface energy of NaCl was high, the coarsening of nanoparticles easily occurred.

Large Ag particles with 100 nm diameter could be seen in Figure 4 as a result of coarsening and agglomerating of Ag particle on NaCl surface. It was possible as changing supporter powder to control nanoparticle size in NPP process

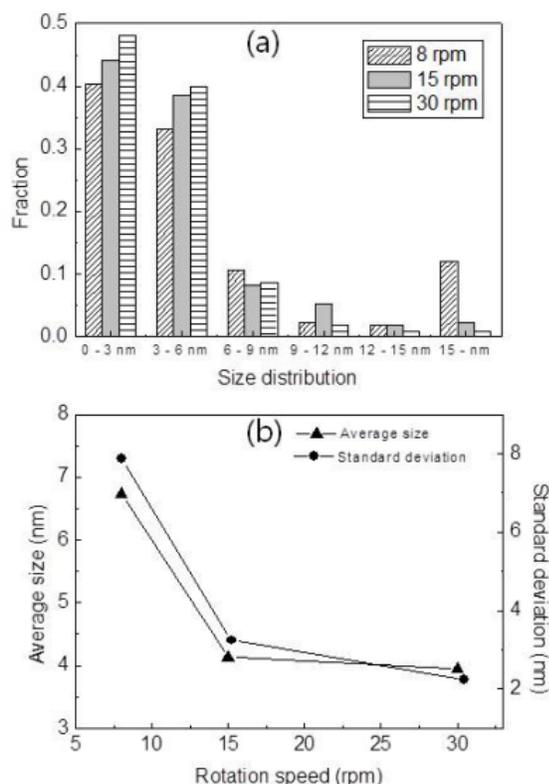


Figure 3 : Size distribution (a) and average size/standard deviation (b) of Ag nanoparticle as a function of stirring speed

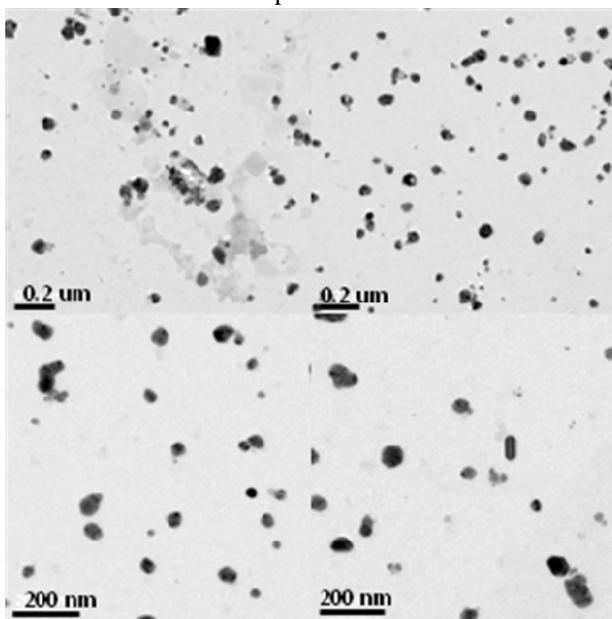


Figure 4 : TEM image of Ag particles which NaCl supporter powder used.

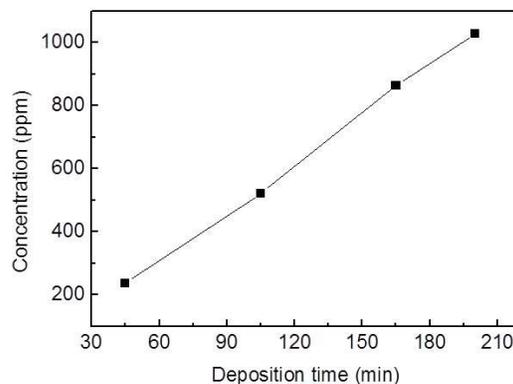


Figure 5 : The concentration of Au particles as a function of deposition time

Finally, the relation between the concentration of nanoparticles in supporter powder and particles size was investigated. Figure 5 showed the concentration of Au nanoparticles in glucose supporter powder as a function of the deposition time. As we knew from Figure 5, the concentration linearly increased as increasing deposition time. We could conclude that the concentration of particles could be easily controlled by changing deposition time in NPP process. We observed Pt, Pd and Au particle size in low concentration and high concentration. Figure 6 showed TEM images of Pt ((a), (b)), Pd ((c), (d)) and Au ((e), (f)). The concentration of Figure 6 (a), (c), (e) was about 500 ppm and that of Figure 6 (b), (d), (f) was about 1,000 ppm. The size of the Pt, Pd and Au nanoparticles on the powder was 2~3 nm and 3~5 nm and 5~15 nm respectively. While the size deviation could be seen in Au nanoparticles, Pt particles were uniform and fine on the whole. Agglomeration and enlargement of the metal nanoparticles are not been observed even though increasing the deposition time on the supporter powder until 1,000 ppm concentration. It could be said that high concentration did not result in coarsening particles. No agglomeration of in even high concentration could be verified in absorption spectrum measurement of Au solution. Absorption peak at about 550 nm could be observed induced by surface plasmon resonance (SPR). A position and width of the normalized SPR peak of Figure 6 (e), (f) were almost same. (not be presented in this article) It meant that the particle size and shape were not changed as increasing concentration because the position and width of SPR peak were strongly related with the particle size and shape. The influence of input weight of supporter powder on nanoparticles will be studied.

4 CONCLUSIONS

Ag, Pt, Pd and Au particles were made under various deposition conditions by NPP process. As stirring speed of supporter powder is high, fine and well-distributed nanoparticles could be obtained because the exposing time

to deposition was too short to agglomerate each other. The supporter powder played an important role to decide the size and shape of nanoparticles. When NaCl supporter powder was used for fabricating Ag particles, the size were dramatically increased compared with glucose supporter powder. However, we verified by TEM and UV-Vis measurement that the concentration of particles in supporter powder did not have an effect to particle size. It would be expected that high quality nanoparticles for chemical catalyst, electronics and agricultures could be made by controlling deposition conditions.

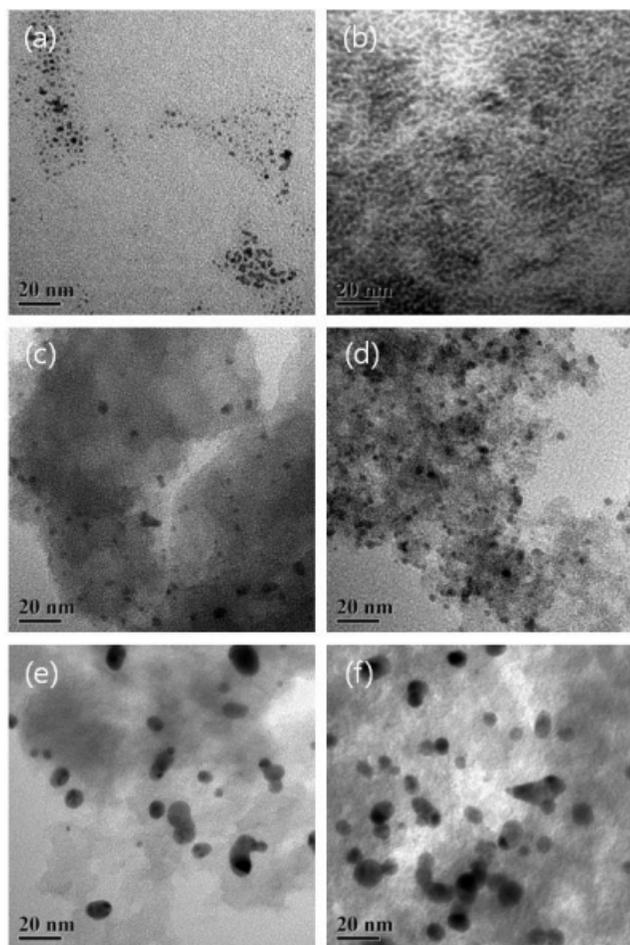


Figure 6 : TEM image of Pt ((a), (b)), Pd ((c), (d)) and Au ((e), (f)) particles. Concentration of (a), (c) and (e) is 500 ppm and that of (b), (d) and (f) is 1,000 ppm

5 ACKNOWLEDGMENT

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