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Size Control Technology of Silver Nanoparticles Using Electron Beam Irradiation

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Introduction

Silver nanoparticles are of great interest to many researchers owing to their ability to be used in many applications such as catalysis, nanoelectronics, optical filters, electromagnetic interference shielding, surface Raman scattering, medical supplies, fabrics, cosmetics, hygiene and kitchen supplies, and electric home appliances.[1,2] Over the past decade, the synthesis of nanoparticles has been an important field of study in chemical science, and a significant contribution to manufacturing techniques of metallic colloids using metal salts as starting materials, such as sol-gels,[3,4] chemicals,[5] electrochemicals,[6] cellulose nanocrystal (CNXL),[7,8] and radiation-induced reduction.[9-13] In particular, radiation-induced synthesis is the most recent technology in this field, and is a promising method because of its many advantages and because of the "green" process achievable with irradiation techniques[14] compared to conventional methods: 1) radiation-induced synthesis is a clean process in which no chemical initiator or catalysts are used; 2) it is very simple and inexpensive; and 3) it is easily able to control the reduction of metal ion, and can be used to obtain metal nanoparticles that are fully reduced, very pure, and in a highly stable state.[3] Several researchers[10-15] have shown the synthesis of nanoparticles by a radiation-induced reduction.[4,5] Radiation-induced reduction is generally the water radiolysis of an aqueous solution with e^-_{aq} and hydrogen atoms produced by water radiolysis using an electron beam (reaction (1)).[6] The hydrated electron e^-_{aq} and hydrogen atoms (reactions (2), (3)) can reduce the dissolved silver ions to silver nanoparticles according to the following reactions:

$$H_2O \xrightarrow{\text{Irradiation}} e^-_{aq}, H\cdot, OH\cdot, H_2O_2\cdot, H_3O, H_2\cdot, OH^-, H^+ \quad (1)$$

$$Ag^+ + e^-_{aq} \rightarrow Ag^0 \quad (2)$$

$$Ag^+ + H\cdot \xrightarrow{\text{reduction}} Ag^0 + H^+ \quad (3)$$

The silver atom Ag^0 easily reacts with Ag^+ and Ag^{2+} ions and progressively grows into stabilized Ag clusters as follows ((4)-(6)):[16]

$$Ag^0 + Ag^+ \rightarrow Ag_2^{+\bullet} \quad (4)$$

$$Ag_2^{+\bullet} + Ag^+ \rightarrow Ag_3^{2+\bullet} \quad (5)$$

$$Ag_2^{+\bullet} + Ag_2^{+\bullet} \rightarrow Ag_4^{2+} \quad (6)$$

It is very important to synthesize silver nanoparticles of a shape and size with a uniform distribution. The nanoparticle size is generally controlled by polymers such as PVA,[17,18] PVP,[19,20] PS,[21] PMMA,[22] PAA,[23] and chitosan.[12]

In this study, we report the large scale synthesis of silver nanoparticles with different sizes prepared through a simple alteration of electron beam conditions, such as the beam energy, current, and absorbed dose.

Experimental

Materials. Silver nitrate ($AgNO_3$, JUNSEI, 99.9%) is used as a precursor without any further purification and poly(vinyl alcohol) (PVA, Mw = 2000) is added to the precursor as a dispersing agent for surface activity. Isopropyl-alcohol (IPA, 99%, DUKSAN Co.) is used as a radical scavenger.

Synthesis of Silver Nanoparticles. The silver nanoparticles are prepared through the electron beam irradiation method. Electron beam irradiation was carried out using an electron accelerator at the Korea Atomic Energy Research Institute (KAERI, Daejeon).

The absorbed doses are 10-300 kGy under the following conditions: (1) beam energy of 0.2-1 MeV, (2) beam current of 0.03-2 mA, and (3) in air and at room temperature.

The absorbed doses are controlled based on the irradiation time, and the calculation equation is the dose [kGy, kJ/kg] = beam energy [MeV] × beam current [mA] × irradiation time [sec]/mass [kg].

The precursor for the nanoparticles is made from a mixed solution of silver nitrate and PVA (0.001 wt %) to which IPA (5 wt %) is added as a radical scavenger. The manufactured sample is then washed with distilled water several times and centrifuged at 12,000 rpm after e-beam irradiation.

Characterization. An analysis of the size, morphology, and structure of the manufactured nanoparticles is carried out using transmission electron microscopy (TEM) and X-ray diffraction (XRD).

Results

Silver Nanoparticle Size Controlled by the Condition of the e-beam. The silver nanoparticle size is controlled variously in accordance with the amount of electron beam energy and current.

The Variance of Particle Size by the Change in the Electron Beam Energy: Figure 1 shows the variance of the particle size by changing the electron beam energy from 0.2 to 1 MeV. The absorbed dose is 30 kGy, and is fixed at 1 mA for the beam current. Only the irradiation time changes.

Uniform silver nanoparticles (< 10 nm) are investigated under a low electron beam energy (0.2 MeV) through a TEM analysis. The results show no significant difference in the particle size between 0.2 and 0.3 MeV.

Silver Nanoparticles Depending on Beam Current: Figures 2 and 3 show the variances in particle sizes at various irradiation currents of 0.03 to 2 mA, a beam energy of 0.3 MeV, and an absorbed dose of 30 kGy.

The silver nanoparticle sizes grow with the increasing beam current. For this reason, the silver nanoparticles agglomerate each silver atom as shown in Eqs. (4)-(6) because of the generated hydrated electrons and hydrogen atoms generated by the e-beam attack the of silver atoms in (1)-(3).

Silver nanoparticle Size Depending on the Absorbed Dose: Figure 4 shows the variance in the particle sizes according to the absorbed dose from 10 to 300 kGy, a beam energy of 0.3 MeV, and a beam current of 1 mA.

The silver nanoparticles grow in size with an increase in the absorbed dose. This is the same result obtained with a changing beam current, and for the same reason, *i.e.*, the increased density of the hydrated electrons and hydrogen atoms at a high dose. This means that the aggregation of silver nanoparticles at a high dose is superior to that at a low dose.

In spite of same the irradiation conditions, the sizes of the silver nanoparticles differ with the concentration of silver precursor in water. This indicates that the sizes of the silver nanoparticles are fixed based on several factors such as the beam energy, beam current, absorbed dose and concentration of the precursor.

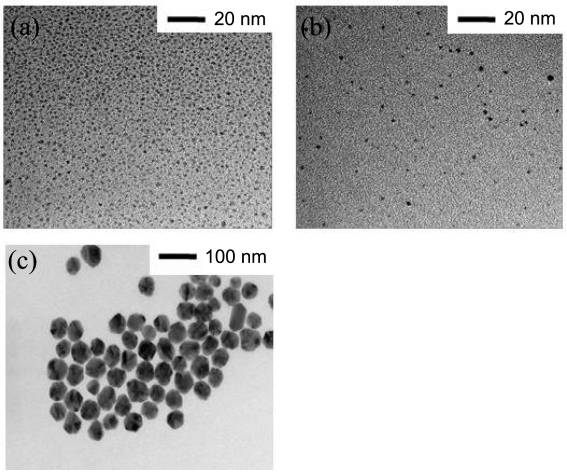

Figure 1. TEM images of the silver nanoparticles at different e-beam energies (absorbed dose, 30 kGy; beam current, 1 mA; and concentration of precursor, 1 wt %): (a) 0.2 MeV, (b) 0.3 MeV, and (c) 1 MeV.

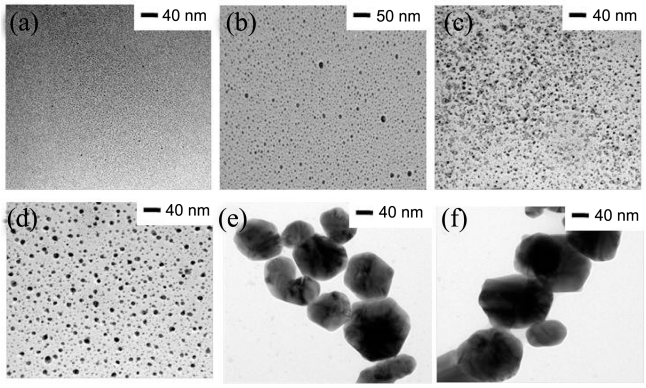

Figure 2. TEM images of the silver nanoparticles at different currents (e-beam energy, 0.3 MeV; absorbed dose, 30 kGy; and concentration of precursor, 10 wt %): (a) 0.03 mA, (b) 0.06 mA, (c) 0.24 mA, (d) 0.48 mA, (e) 1 mA, and (f) 2 mA.

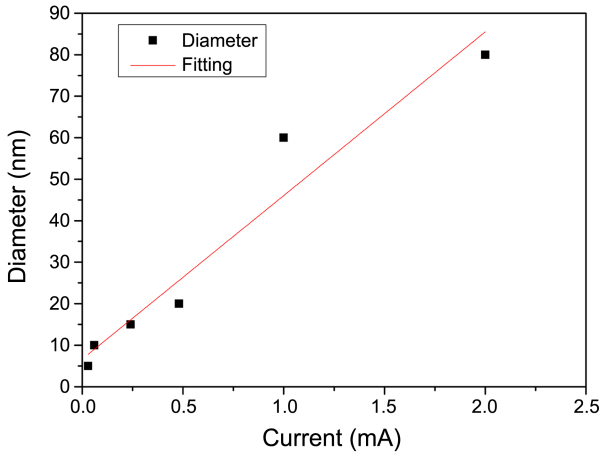

Figure 3. Linearity of e-beam current *vs.* particles size.

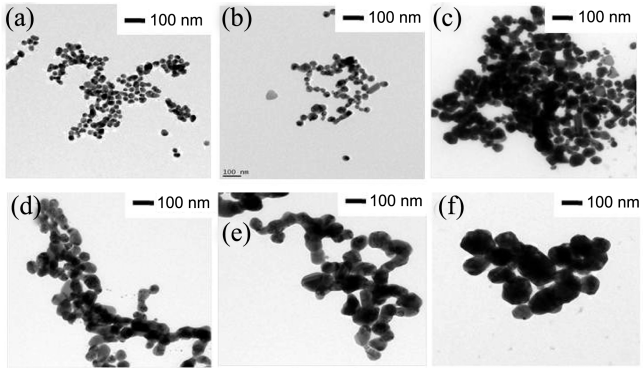

Figure 4. TEM images of the silver nanoparticles the absorbed doses (e-beam energy, 0.3 MeV; beam current, 1 mA; and concentration of precursor, 7 wt %): (a) 10 kGy, (b) 30 kGy, (c) 50 kGy, (d) 100 kGy, (e) 200 kGy, and (f) 300 kGy.

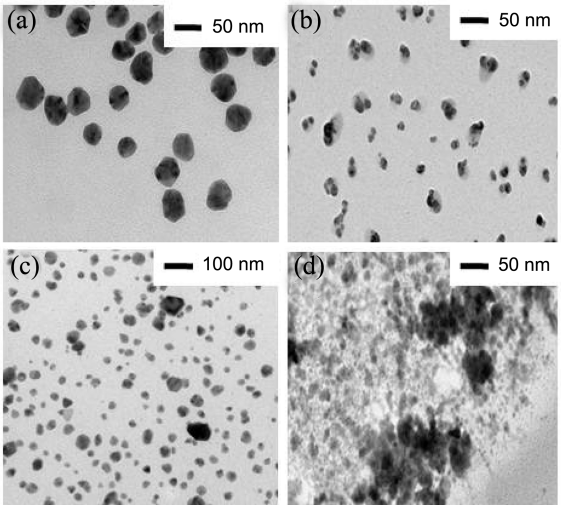

Figure 5. TEM images of silver nanoparticles as dispersing agents: (a) Poly (vinyl alcohol) (PVA), (b) glycerol, (c) poly (vinylpyrrolidone) (PVP), and (d) gelatin.

Synthesis oF Silver Nanoparticles at a Uniform Size. In the previous results, the silver nanoparticles agglomerated together owing to the interfacial attraction by increasing the total absorbed dose and beam current. To prevent the aggregation of silver nanoparticles, various dispersing agents are used.

Using a dispersing agent, it is possible to decrease the interfacial attraction of each silver nanoparticle. The dispersing abilities of poly(vinyl alcohol) (PVA), glycerol, poly(vinylpyrrolidone) (PVP), and gelatin are compared through the uniformity of the silver nanoparticles.

PVA is a very effective dispersing agent as shown in Figure 5. The PVA is added to the precursor solution at the start of the reaction or continuously during the reaction.

Small and uniform silver nanoparticles are manufactured using PVA as the dispersing agent. It is thought that PVA can most effectively control the silver nanoparticle size by preventing the agglomeration of silver nanoparticles in an aqueous solution.

The XRD pattern in Figure 6 demonstrates that the silver nanoparticles obtained in this research contain no impurities (such as oxides) in the FCC face centered cube.

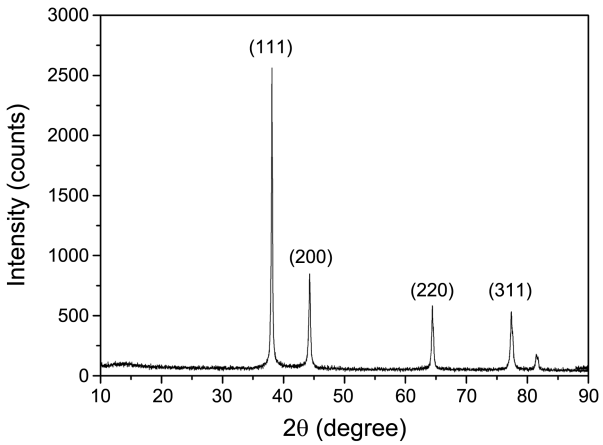

Figure 6. XRD pattern of silver nanoparticles.

In this research, the manufacturing of silver nanoparticles using an electron beam is easy, fast, and highly productive, and it is possible at room temperature with no chemical residuals. Its various advantages therefore make this an important method for manufacturing nanoparticles such as silver, copper, and platinum.

In particular, despite the use of electron beam irradiation, the results show that this method makes it possible to produce silver nanoparticles at low cost since low beam energy and low doses are used. This means that middle and high-energy electron beam accelerators are very expensive, but a low-energy electron beam accelerator has a relatively low cost of around 4-5 times, and mass production for a flow reaction without the need for extra radiation shielding is possible.

Conclusion

Silver nanoparticles suitable for application in electronic printing, catalysts, photonics, and so on were successfully fabricated through e-beam treatment on two types of electron accelerators.

Silver nanoparticles are smaller at a low e-beam energy of 0.2 MeV than at a high e-beam energy of 1 MeV owing to the large electron density of the high e-beam energy. In addition, the sizes of the silver nanoparticles increase at a high beam current and absorbed dose. For this reason, silver nanoparticles are agglomerated by interfacial attraction, whereby they increase with an increase in beam current and dose. This results in a high electron density in an aqueous solution including a silver precursor.

To prevent the aggregation of silver nanoparticles, various dispersing agents are used, such as PVA, glycerol, PVP, and gelatin. Of these, PVA has the best dispersing ability, by which it is easy to control the particle size and uniformity of the silver nanoparticles.

Finally, this e-beam method is particularly valid for silver nanoparticles because it makes possible a high productivity and the use of no chemical agents, and is an easy, fast, and eco-friendly process.

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