METAL NANO-PARTICLE SYNTHESIS BY USING PROTON BEAM*
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Abstract
Many scientists have studied metal nano-particles for newly known optical, electronic and chemical properties. The unique properties of nano-particles have a tendency to relate the particle size and shape. Electron beam has been used for the nano-particle synthesizing and many results were published. Study of nano-particles synthesized by using proton beam is still in the early stages however study for gold, silver, platinum and cobalt nano-particle was in progress. 100 MeV proton linear accelerator, which is by proton engineering Frontier Project (PEFP), Korea Atomic Energy Research Institute (KAERI), is scheduled to be completed by 2012. Study of nano-particle synthesis by using proton beam will become active due to the completion of 100 MeV proton accelerator and it can be mass-produced by proton beam irradiation. Mechanisms of metal nano-particles synthesizing by using proton beam irradiated condition, such as dose rate, beam irradiation time, etc and size controlled studied according to the present or absent of additive were not clear. In this study, we investigated the changes of size and shape for metal nano-particles produced using proton beam depending on the condition of proton beam irradiation and present or absent of additives by Transmission Electron Microscopy (TEM) and UV/VIS spectrophotometer.

INTRODUCTION
It has been commonly known that nano-sized metal material differ specifically in their physical and chemical properties from the bulk material and the metal nanoparticles are related not only to particle size but also to particle shape as well [1]. The fabrication of nano-size materials with strict control size, shape, and crystalline structure has inspired the application of nanochemistry to numerous fields including catalysis, medicine, and electronics. Synthesis methods for nanomaterials are various, such as simple chemical reduction, electrochemistry, photo chemistry, templating seeding, physical process, and using radiation [2-4].

According to reports, research of nano-particle synthesis using proton beam is limited to some metals [5-7]. The principle of producing metal nano-particles via proton beam irradiation, proton beam produced hydroxyl radical by stimulate OH⁻ functional groups of water molecules in aqueous solution and it makes a reduction of the metal. However its exact mechanism is still unknown. It has many advantages produced nano-particles using proton beam irradiation. Because there is no need to use additional reducing agent, radical generated from water molecules. It is very important to simplify the nano-particle separation process.

In this study, we examined the controlled of size and shape of metal nano-particles depending on the variable condition by proton beam irradiation.

EXPERIMENTS
Materials
Gold chloride (HAuCl₄), silver nitrate (AgNO₃), chloroplatinic acid hexahydrate (H₂PtCl₆·H₂O) polyvinyl alcohol (PVA, average molecular weight of 40,000), cetyltrimethylammonium bromide (CTAB) and NaOH were used as purchased from Sigma Aldrich Korea.

Proton Beam Irradiation and Sample Analysis
Samples were irradiated proton beam from the MC-50 cyclotron (Scanditronix, Sweden) at the Korea Institute of Radiological & Medical Sciences (KIRAMS) and 20 MeV proton linear accelerator at Korea Atomic Energy Research Institute (KAERI). All the metal aqueous solution was irradiated by proton beam at atmospheric pressure and room temperature to synthesize metal nanoparticles. The solution was mixed gently for a 10 sec to 1 minute and 1 ml of the mixed solution was transferred to a 1.5 ml tube for proton beam irradiation. The color of the resulting solution varied from pink to violet, brown or black depending on preparation sample conditions. Absorbance spectra were obtained using a UV/VIS spectrophotometer (UV-2550, shimadzu) and transmission electron microscopy analysis were carried out in a KAERI.

RESULTS
Pt Nano-particle Synthesis by using Proton Beam Irradiation
We were carried out some experiments to find factors that control the size of pt nano-particles. First, we were making the experimental device to find out the effect of the energy and linear energy transfer (LET) to nanoparticle synthesis. Its thickness is 2mm and it can stack a several sheet. As shown in Figure 1, the particle size seems to be smaller pattern by decrease energy and increase LET. However, when it reaches a specific region is increasing in the size of the particles. Also we found that changing the shape of the particles depending on the type of surfactant. As surfactant, when using CTAB and SDS, the shape of platinum nano-particles is a cubic and wire, respectively (Figure 2).
Au Nano-particle Synthesis by using Proton Beam Irradiation

HAuCl₄ aqueous solution was irradiated proton beam with a mean current of 10 nA and dose rate 0.5 Gy/sec for 30 min. Proton beam irradiated HAuCl₄ aqueous solution, color was converted from yellow to pink coincide with producing nano-particles. Figure 3 shows UV/VIS absorption spectra of the gold nano-particles containing solution after proton beam irradiation. As shown Figure 3, an absorption band appeared at around 550 nm, which corresponding to the surface Plasmon absorption band of gold nano-particles, and peak height of 30 min irradiated group is higher than 20 min irradiation group. The case of metal nano-particles, in general, they has a pattern that growing particle size increases absorbance intensity. In case of gold nano-particles, location of Plasmon band changes depending on the shapes and particle sizes. The result suggests that the particle size was increased the longer irradiation time and the higher total absorbed dose.

Next, we carried out proton beam irradiation after added the NaOH and/or CTAB in gold aqueous solution. Although the initial color of Au aqueous solution is light yellow, the color was converted to colorless after the addition of NaOH. Here, the addition of CTAB, the color of gold aqueous solution is reduction on yellow again. Figure 4 shows the results for UV/VIS spectrum and TEM image of gold nanoparticle produced by proton beam irradiation added the NaOH concentration of 0.5 M and CTAB concentration of 0.5 to 4 mM in Au solution.

As a Figure 4, CTAB concentration is important in determining the shape of the nano-particles. CTAB concentration is higher, the absorption band blue-shifted and a broad shoulder was clearly noticeable. The broad structure emerged in the visible to the infrared region was assigned to the surface Plasmon absorption band of rods.

Figure 1: LET and energy effects of platinum nano-particle synthesis using proton beam. A. Slice sample stack and resulting proton beam irradiation. B. Particle size of various irradiation conditions.

Figure 2: Surfactant controlled the shape of platinum nano-particles. A. CTAB. B. Sodium dodecyl sulphate (SDS).

Figure 3: UV/VIS spectra of Au nano-particles producing by proton beam irradiation.

Figure 4: UV/VIS spectra and TEM images of difference conditions of NaOH and CTAB concentration. A. UV/VIS spectrum. B. TEM image.
and wires [8]. It should be noted that the concentration of CTAB in reaction condition was just below the critical Micelle concentration (CMC) of CTAB, which is known to be 0.001 M at temperatures below 301K [9].

One drop of the reaction mixture was placed on a carbon-coated Cu grid for TEM analysis (Figure 4B). TEM images that correspond to the Au nano-particles produced under various CTAB concentrations. One mM CTAB concentration, TEM images indicate high yields of well-defined Au nano-particles with an average diameter of ~20 nm. They included spherical shape, tadpole-shaped nanorods, and nanowires. Two mM CTAB concentration, TEM image of one-dimensionally grown Au nanowires were easily observed.

Figure 5 shows the UV/VIS spectra and TEM images of effect of irradiation time of the proton beam on the formation of gold nanomaterials. A. UV/VIS spectrum of 1mM concentration of CTAB. B. TEM image of Figure 5A. C. UV/VIS spectrum of 2mM concentration of CTAB. D. TEM images of Figure 5C.

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**REFERENCES**