Effect of additives on the formation of bismuth nanoparticles by polyol process

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Formation of bismuth nano-particles by polyol process have been studied in terms of the effect of additives on its size and shape. Bismuth trichloride solved in ethylene glycol was reduced at high temperature with the existence of poly(vinylpyrrolidone) (PVP) and ferric chloride. Spherical particles were mostly formed with the solitary addition of PVP. Sphere size was decreased from 400 to 200 nm with increasing amount of the PVP. Addition of larger weight-average molecular weight (Mₚ) of the PVP decreased the sphere size slightly. On the other hand, hexagonal or rectangular plate-like particles were obtained at a high number ratio over 70% by the co-addition of ferric chloride with the PVP. Plate size and the fraction of plate-like particles tended to increase slightly with the increase of amount of the PVP. The plate size also increased with increase of molecular weight of the PVP and square plate-like particles larger than 1 micrometer were obtained with the addition of the large molecular size of PVP (Mₚ ~1,300,000). Adequate amount and size of PVP tended to decrease totally the growth speed of particles and to suppress coalescence with each other, and ferric ions suppressed the growth speed toward the c-axis by alternative re-oxidization of bismuth metal.

Key-words : Bismuth, Spherical nanoparticle, Plate-like nanoparticle, Polyol process, Poly(vinylpyrrolidone)

1. Introduction

Transparent materials dispersed metal nanoparticles are of great interest for the optical application. For example, ellipsoidal silver nanoparticles oriented glass composites and aluminum nanowires aligned substrates are respectively used as absorption-type and reflection-type polarizer due to their optical anisotropy developed from their anisotropic shapes. Bismuth is a semimetal with small band overlap and a very anisotropic electron effective mass-tensor, so that bismuth shows optical anisotropy even when it has a nanosized spherical shape and the anisotropy is enhanced when the shape becomes plate-like owing to the effect of geometric anisotropy. Bismuth nanoparticles are expected as a candidate of dispersed materials. Formation of bismuth nanoparticles has been extensively studied several kinds of shape such as spheres wires, ribbons, rods, plates and so on. Polyol and solvothermal processes are usually applied with some modifications of starting materials, solvents for reduction and polymer templates, and under some conditions of pressures using autoclave reactor or magnetic fields. The mechanism of anisotropic growth is not clear yet. On the other hand, Chen et al.11) and Xia et al.1) reported the anisotropic growth and the growth mechanism of platinum and palladium nanoparticles with the existence on ferric ions on the polyol process. The ferric ions, therefore, have a potential to be effective against anisotropic growth of nanoparticles of the other metallic elements. In the present paper, we have studied the effect of additives both poly(vinylpyrrolidone), PVP, and ferric chloride on the formation of bismuth nanoparticles on polyol process. The influence of the additives, molecular weight and amount of PVP and co-existing ferric ions, on the size and shape is discussed.

2. Experimental procedure

Bismuth nano-particles were prepared by the polyol process,1,12) which was similar to that reported by Wang and Kim.3) 70 mg of bismuth trichloride (Kojundo chemical, 99.99%) was dissolved in 50 mL of ethylene glycol (Kishida, 99.5%) with sodium hydroxide (Kishida, 95%) and poly(vinylpyrrolidone) (PVP) under a nitrogen atmosphere. The amount of sodium hydroxide was 4.5 times or more in mol than that of bismuth trichloride according to the reaction formulae of the bismuth formation.3) When an addition of sodium hydroxide was less than the amount for full reaction, particles having irregular shape, which were chemically unstable, were formed, while the addition larger than that amount brought stable spherical particles and almost constant size. PVP is used commonly as capping molecules to inhibit the aggregation of atoms and as a template to control the size and shape of the nanoparticles. Weight-average molecular weights (Mₚ) of the PVP used were ~10,000 (Aldrich), ~30,000 (Wako chemical), ~55,000 (Aldrich) and ~1,300,000 (Aldrich), respectively. Amount of the PVP was varied from 0 to 10 grams. The mixture was placed in a three-necked flask fitted with a reflux condenser, then heated to 190–193°C over 1.5 h and kept at the temperature for 2 h under the nitrogen flow (100 mL/min). The black bismuth nano-particles were obtained above ~180°C at the heating step. The resultant was poured into ice-cooled ethylene glycol (75 mL) and then collected by centrifugation. The nano-particles were rinsed out by sonication and centrifugation in ethanol for several times. The final products were dispersed and kept in ethanol. Plate-like particles were prepared by adding 25 mg of ferric chloride with

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extra sodium hydroxide into the starting mixture. Crystal structure of the nano-particles was characterized by powder X-ray diffraction from 15 to 80°, using Cu-Kα radiation on an X-ray diffractometer (Rigaku, Ultima IV). Scanning electron microscopy and its chemical analysis was performed by an electron micro probe analyzer (JEOL, JXA-8100).

3. Results and discussion

XRD patterns of two products synthesized with (plate-like particles) and without (spherical particles) addition of ferric chloride are shown in Fig. 1. All of the peaks in the XRD patterns can be readily indexed to the pure rhombohedral phase (JCPDS 05-519/44-1246) as same as the spherical particles reported in previous work.1),2)

Figure 2 shows SEM images of spherical bismuth nanoparticles prepared by adding only the PVP ($M_w \approx 55,000$). Small amount of particles having plate-like shape were observed in some case, when the ferric chloride was not introduced. Particles coalesced with each other when the PVP was not used. Diameter of the spheres gradually decreased from $\sim$400 nm (1 g) to $\sim$200 nm (>5 g) with increasing amount of the PVP. Polymer molecules called capping molecule inhibits the aggregation of bismuth atoms and clusters, that is, Ostwald ripening,13) resulting in isolated smaller particles. In the present formation, PVP molecules might act as a capping molecule as same as past studies about formation of Au, Ag and the other metal nanoparticles by solution phase synthesis.14) The suppression of growth rate by capping molecule will be influenced not just by the amount of molecules, but also by the spatial molecular size, i.e., the molar weight. Therefore, SEM images of the nanoparticles prepared by using 1 g of PVP which has different molar weight are shown in Fig. 3. Spherical particles were formed with the addition of PVP having molecular weight, $M_w$, larger than 30,000. The particle size, however, almost stayed constant above the weight, while it became a few times larger and some particles having irregular shape were formed when the PVP with $M_w \approx 10,000$ was used. Molecular size of PVP ($M_w \approx 10,000$) is supposed to be about 10 nm at most, so that bismuth atoms and clusters would aggregate easier through the voids among the molecules resulting in larger particles as compared with the other larger molecules.

Effects of additives and conditions on the size and shape has been reported3) and so on. For example, Wang et al.3) studied the effect of sodium hydroxide on the shape of particles in the polyol process. They reported triangular nanoparticles or nano-wires were formed with an addition of appropriate amount of it. On the other hand, Wang et al.8) prepared bismuth nanowires by using sodium bismuthate (NaBiO3·2H2O) with the PVP of $M_w \approx 1,300,000$ by polyol process in an autoclave reactor. Introduction of acetone in ethylene glycol led formation only spherical particles. The annihilation of anisotropic growth was deduced to the dilution of the PVP. Non-spherical particles were also produced by the other processes such as the solution–liquid–solid (SLS) growth,5) reaction in an autoclave under magnetic field10) and so on.7) Thus in the other processes, the PVP suppressed both the growth speed, and growth on a certain crystal surface resulting in anisotropic shape of particles. In the present experiment, however, the PVP suppressed growth speed as same as the past reports, but had a small effect on the anisotropic growth in any condition, although the reason is not clear yet.

On the other hand, hexagonal or rectangular plate-like particles were formed when ferric chloride was co-doped with PVP as shown in Fig. 4. The thickness was about 50 nm in any case. Number ratio of plate-like particles to spherical particles was a few percent when the chloride was not introduced. The ratio increased into $\sim$70% with the increasing FeCl3/BiCl3 mole ratio of above $\sim$0.7. Chlorine and iron ions were not detected in spherical particles from the analysis using EPMA within its detection limit, while iron atoms were detected faintly in plate-like particles, but the amount of iron atoms could not be esti-
The effect of ferric ions was reported on the growth of palladium,12) or platinum and silver11) nanoparticles. On the growth of palladium nanoparticles, ferric species act as an effective etchant to a certain crystal surface due to the difference of the standard potentials of the redox pairs: Fe(III) + e⁻ → Fe(II), \( E' = 0.77 \) V and PdCl₄²⁻ + 2e⁻ → Pd + 4Cl⁻, \( E = 0.59 \) V. Since the standard potential of the reduction of bismuth ion (Bi(III) + 3e⁻ → Bi(0)), \( E = 0.317 \) V, is smaller than that of ferric ion as same as the reduction of palladium. The anisotropic growth should be enhanced on the formation of bismuth nanoparticles according to the mechanism of the effective etching by re-oxidization. Wang et al.⁹ reported the anisotropic growth of bismuth particle by reduction reaction with ferric ions in autoclave. Cubical particles were formed in their experiment. Although the final shape of the particles differs from the present result, the anisotropic growth appeared only the existence of ferric ions. Moreover, the rate of effective etching seems to be comparative or slower than that of the growth rate. Because the aspect ratio of plate-like particles was affected by the amount of PVP. The PVP suppress the growth rate of the particle as mentioned above, so that the anisotropic etching became more apparent with larger addition of it resulting in the increase of the aspect ratio, although the reason of the change from hexagonal-like to rectangle shapes is not clear yet.

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