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Fabrication of Spherical Bi Particles during Polyol Synthesis using a Bismuth(III) Carbonate Precursor

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Keywords: Polyol Synthesis, Bi particle, bismuth(III) carbonate, particle shape, processing temperature.

Abstract. Spherical Bi particles were fabricated through a polyol synthesis using a zinc bismuth(III) carbonate precursor, and the effects of processing temperature and time on the morphology and composition of the resulting particles were evaluated. It was determined that longer processing times or higher processing temperatures resulted in the gradual conversion of as-formed bismuth hydroxide into spherical elemental bismuth via bismuth glycolate. The temperature for the effective synthesis of spherical Bi particles under these conditions was 230 °C.

Introduction

Bismuth is used in the pharmaceutical, cosmetic, and pigment industries, and it is a non-ferrous metal that is applied for casting and galvanizing, an alloying element that replaces lead, and a constituent of solder alloy in the metal industry. Moreover, Bi has increasingly been noticed for its environmentally friendly lubricant properties, excellent thermoelectric nature, unusual electron transfer properties, electro-optical properties, and large magnetoresistance [1-7].

In this study, Bi particles were fabricated through a polyol synthesis using a zinc bismuth(III) carbonate precursor; spherical Bi particles were obtained by tuning processing parameters such as temperature and reaction time.

Experimental

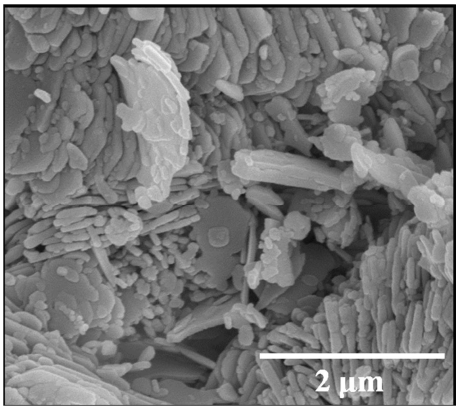
Zinc bismuth(III) carbonate basic (CBi_2O_5, Sigma-Aldrich) was used as the precursor, while propylene glycol ($C_3H_8O_2$) was the polyol solvent. For the synthesis, zinc bismuth(III) carbonate basic (5.1 g) was completely dissolved in 100 ml of propylene glycol at ambient temperature using a rotating magnetic stir bar. The resultant solution was poured into a three-neck round flask and heated to a specific temperature using a heating mantle. The polyol solution was then heated under continuous stirring beyond the boiling point of the solvent (188 °C); the evaporated propylene glycol was recycled via condensation using a cooling tower. The heating rate and mixing speed were held constant through all experiments. The reaction period at the specific synthesis temperature varied from 4 to 18 h. The flask was removed after the specified time and cooled to ambient temperature.

The resultant propylene glycol solution, which contained particles, was decanted after centrifugation and then methanol was poured into the slurry. The resulting solution was exchanged with methanol by repeating this procedure three times. After drying the final solution in a low-vacuum chamber at ambient temperature, the Bi powders were gathered. The morphology and sizes of the resulting particles were evaluated via scanning electron microscopy (SEM).

Results and Discussion

It is proposed that the electrons that are required to reduce the Bi ions during the polyol synthesis are provided by the conversion of the hydroxyl groups to carboxyl groups as follows [8]:

$$–CH(OH)–CH(OH)– \rightarrow 2 >C=O + 4H^+ + 4e^-$$



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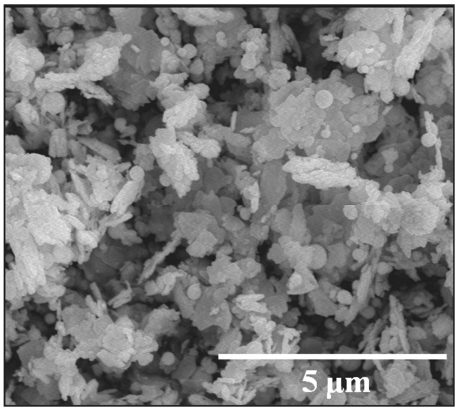

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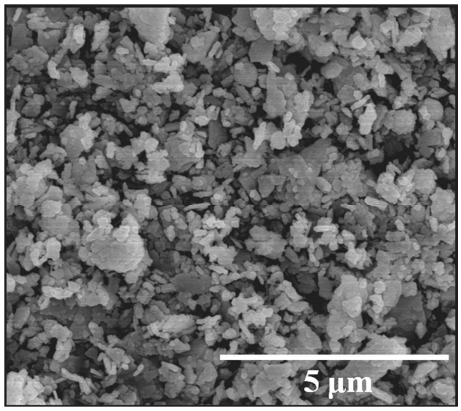
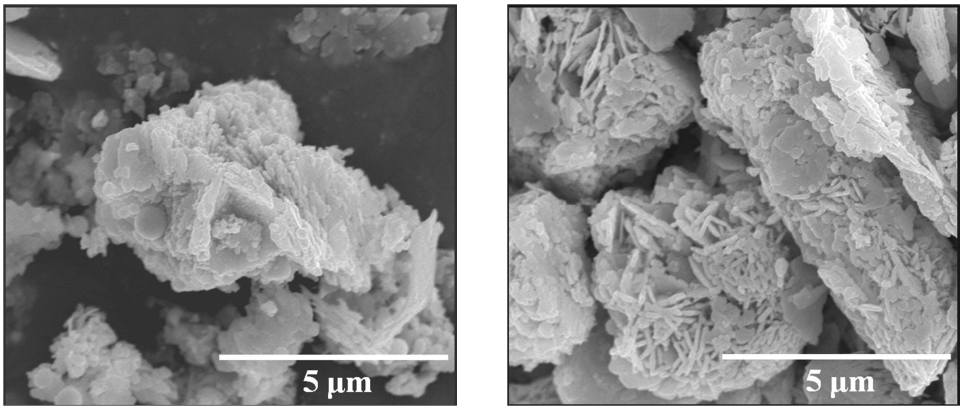


(c)

Fig. 1. SEM images of the Bi particles obtained via polyol synthesis in propylene glycol at 188 °C with processing times of (a) 4 h, (b) 8 h, and (c) 18 h.

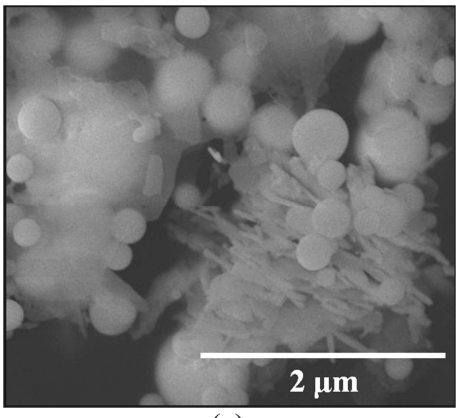
Fig. 1 shows SEM images of the Bi particles that were synthesized at 188 °C with varying processing times. After 4 h (Fig. 1a), most of the synthesized particles were platelet-shaped, while some were elongated spheres. This result implies that the particles mainly comprise bismuth hydroxide [9]. Since the platelet-shaped particle stacking was relatively regular in comparison with the other samples, it was determined that the platelet-shaped particles adhere to the flat surfaces during volume shrinkage due to drying. However, the specimen synthesized over 8 h (Fig. 1b) showed a mixed microstructure comprising spheres and non-stacked platelets that were of a similar size to those obtained after 4 h (note that the magnification is different). In similar experiments, the platelet and spherical particles were indexed as bismuth glycolate with an approximate composition of $Bi_2(EG)_3$ and elemental bismuth, respectively [9]. Increased time at 188 °C induced the conversion of bismuth hydroxide into bismuth glycolate and elemental bismuth. The distribution of particles was greatly irregular, which is due to a significant reduction in inter-particle interactions. This difference in interactions is caused by the increasing number of spherical particles. It is highly likely that spherical particles, which do not have a stable plane, tend to physically hinder strong adhesion between the platelet particles during drying. The specimen processed for 18 h (Fig. 1c) featured smaller particle sizes and more dispersed distribution; also, the number of elongated or spherical particles increased. This result indicates that the bismuth glycolate slowly converted to elemental bismuth with increased processing time. The bismuth glycolate intermediates more readily decompose and release free Bi ions, which are rapidly reduced by propylene glycol molecules, with increasing temperature. If the specific surface of a cluster was not the preferred orientation, the cluster formed by reduction would be spherical since it has the lowest surface energy. In summary, the platelet-shaped bismuth hydroxide particles that were initially synthesized at 188 °C slowly converted to elongated or spherical elemental bismuth via bismuth glycolate, as the processing time increased.



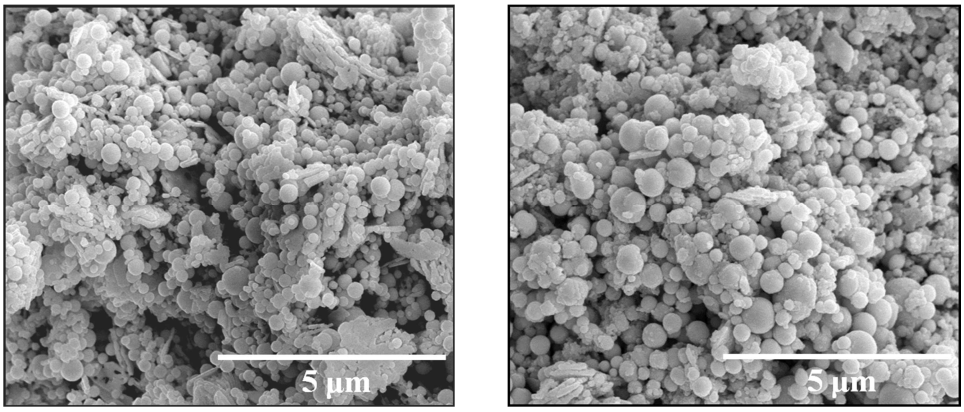
(a) (b)

Fig. 2. SEM images of Bi particles obtained via polyol synthesis in propylene glycol for 4 h at processing temperatures of (a) 210 °C and (b) 220 °C.

To obtain more spherical Bi particles through the polyol synthesis, the temperature was gradually increased. Fig. 2 shows SEM images of Bi particles synthesized at 210 °C and 220 °C for 4 h. Although a few spherical particles were observed, most of the nanoparticles remained platelet-shaped, which is mainly due to the short synthesis time. As a result, there was significant inter-particle interaction.



(a)



(b) (c)

Fig. 3. SEM images of Bi particles obtained via polyol synthesis in propylene glycol at 230 °C for (a) 4 h, (b) 8 h, and (b) 18 h.

To fabricate the spherical particles in a more effective manner, the synthesis temperature was increased to 230 °C. Fig. 3 shows SEM images of Bi particles synthesized at 230 °C with different processing times. After just 4 h (Fig. 3a), a significant number of almost fully spherical Bi particles

were formed simultaneously with high-aspect-ratio ribbons of bismuth hydroxide. Thus, it was determined that increasing the processing temperature is a reasonably effective method of forming spherical Bi particles when compared to lower temperature syntheses with identical processing times (Fig. 2). Although some platelet particles were still present, a significant number of Bi particles converted into a spherical shape with increased processing time at 230 °C, as verified by Fig. 3(b). After 8 h of processing, the sizes of the particles deviated significantly and some particles agglomerated into a cluster. Fig. 3(c) shows an image of Bi particles that were processed for 18 h: There were an insignificant number of platelet particles, agglomeration was considerably suppressed, and the size deviation increased slightly. Accordingly, a higher processing temperature and longer processing time gradually increased the number of spherical Bi particles obtained from the polyol synthesis in propylene glycol using zinc bismuth(III) carbonate basic.

Summary

The polyol synthesis of spherical Bi particles from a zinc bismuth(III) carbonate precursor was performed. It was verified that a longer processing time or higher processing temperature resulted in the gradual conversion of the as-formed bismuth hydroxide into spherical elemental bismuth via bismuth glycolate, which indicates that the bismuth glycolate intermediates more completely decompose and release free Bi ions with increasing temperature and time. From the results regarding processing temperature, the temperature for the effective synthesis of spherical Bi particles was determined to be 230 °C.

Acknowledgement

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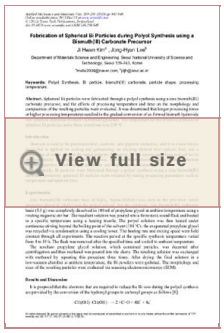

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