

Effects of pH on Tin Nanoparticles Prepared Using a Modified Polyol Synthesis

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Abstract. The effects of pH on the morphology and size distribution of Sn nanoparticles (NPs) synthesized using a modified polyol method were investigated. An ammonia solution was used to increase the pH, and at pH values ranging from 10.3 to 12, the average size and size deviation of the synthesized Sn NPs decreased with increasing pH. We believe that higher pH enhances the rate of reduction of Sn ions during the synthesis, resulting in an increase in nucleation. Therefore, the concurrent formation of many nuclei might be the main cause for the reduction in average particle size and for the enhancement in size uniformity.

Introduction

As interest in nanoscale material systems has increased, the synthesis, characterisation, and application of metallic nanomaterials made of Au, Pt, Pd, Ag, and Cu have been subjected to extensive studies in the past decade [1]. However, because such distinctive properties have been discovered in other metallic nanomaterials as well, many studies on Sn nanomaterials, for example, have been recently conducted [2,3]. Among the diverse approaches to synthesizing metallic nanoparticles (NPs), wet chemical routes are highly attractive because of the ease with which the various variables in the process can be adjusted. In particular, the modified polyol process, which entails the decomposition of metal precursors and the subsequent reduction of metal ions using a strong reductant in the polyol solvent, is advantageous in terms of its fast reaction time and the use of ambient conditions. Various process parameters such as the type of precursor or solvent, the type or molecular weight of the capping agent, and the concentrations of various agents are important parameters affecting the modified polyol process. However, reports on the effect of the pH of the reaction solution on the NPs formed are rare, with the exception of a few extensive studies on the synthesis of Ag and Cu NPs. In this study, therefore, the effects of pH on the morphology and size distribution of Sn NPs synthesized using the modified polyol process were analysed.

Experimental

Tin(II)-2-ethylhexanoate ($C_{16}H_{30}O_4Sn$, ~95%) and sodium borohydride ($NaBH_4$, 99.99%) were employed as the precursor and reducing agent, respectively, and diethylene glycol (DEG) was selected as the polyol solvent. 1,10-Phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) and trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) were used as the capping agent and surfactant, respectively, to suppress the agglomeration of the synthesized Sn NPs. To adjust the pH of the polyol solution, aqueous ammonia (28–30%, Samchun Pure Chemical Co., Ltd.) was used. All chemicals except the ammonia solution were supplied by Sigma-Aldrich Co. and used as received. Sn NPs were synthesized in air at room temperature by injecting tin(II)-2-ethylhexanoate into a DEG solution containing sodium borohydride, 1,10-phenanthroline, and trisodium citrate. To prepare the DEG solution, 2 g of sodium borohydride, 1 g of 1,10-phenanthroline, and 0.1 g of trisodium citrate were completely dissolved in 100 mL of DEG at room temperature with magnetic stirring for 80 min. Then, the ammonia solution was added dropwise to the prepared solution to vary the pH of the solution to 10.5, 11, or 12, and the solution was then left for 4 h. Finally, 2 mL of tin(II)-2-ethylhexanoate was directly injected into the prepared solution at the rate ~4.5 mL/min using a dispenser. The DEG solution containing Sn NPs was subjected to continuous magnetic stirring for 30 min from the moment of injection, and sampling was carried out every 10 min.

The sample for transmission electron microscopy (TEM, Tecnai 20, FEI Company) was prepared by placing a few drops of the solution containing Sn NPs onto copper grids coated with a carbon film. Because drying of DEG takes a long time owing to its low volatility, dried Sn NPs were prepared in a vacuum chamber maintained at room temperature. To confirm the identity of the synthesized NPs, selected area electron diffraction (SAED) measurement was also carried out during the TEM analysis. Images of the Sn NPs dried in a beaker were obtained using a scanning electron microscope (SEM, Hitachi S -4700, Hitachi Ltd.).

Results and Discussion

Fig. 1 shows a representative TEM image of the Sn nanoparticles synthesized for 20 min using the modified polyol process described above but without adding the ammonia solution. The sample obtained without adding ammonia was used as a reference for the samples synthesized with ammonia. The pH of the solution obtained without adding ammonia was 10.3 before the Sn precursor was injected. Irregularly shaped NPs with relatively uniform sizes ranging from 100 to 200 nm were observed. Moreover, the NPs were aggregated and partially agglomerated.

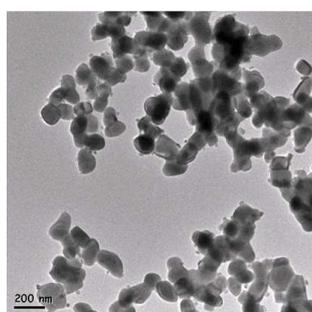


Fig. 1. TEM image of the Sn NPs synthesized using the modified polyol process, i.e., without adding ammonia solution (pH 10.3).

The SAED patterns and a magnified TEM image of the Sn NPs synthesized at pH 12 are shown in Fig. 2. Analysis of these patterns confirmed that the synthesized NPs were β -Sn. The presence of clear ring fringes indicates that crystallisation occurred along different growth planes in the groups of NPs. The high-magnification TEM image shown in Fig. 2(b) indicates the presence of crystalline structures. Moreover, the interplanar distance and thickness of the capping layer were measured to be 0.29 and 4.9 nm, respectively. The distance of 0.29 nm corresponds to the interplanar distance between (200) planes of β -Sn.

Fig. 3 shows the TEM images of the Sn NPs synthesized at different pH values for various reaction durations. As shown in Fig. 3, both the pH and reaction time have significant effects on the size distribution of the Sn NPs. In addition, the pH also had a marked influence on the

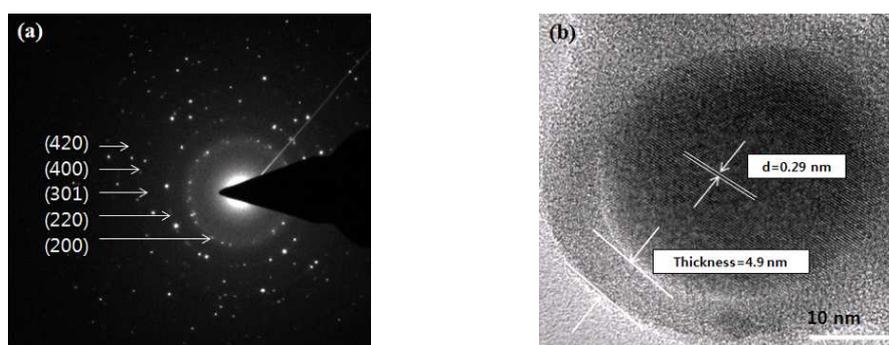


Fig. 2. (a) SAED patterns and (b) a magnified TEM image of the synthesized Sn NPs.

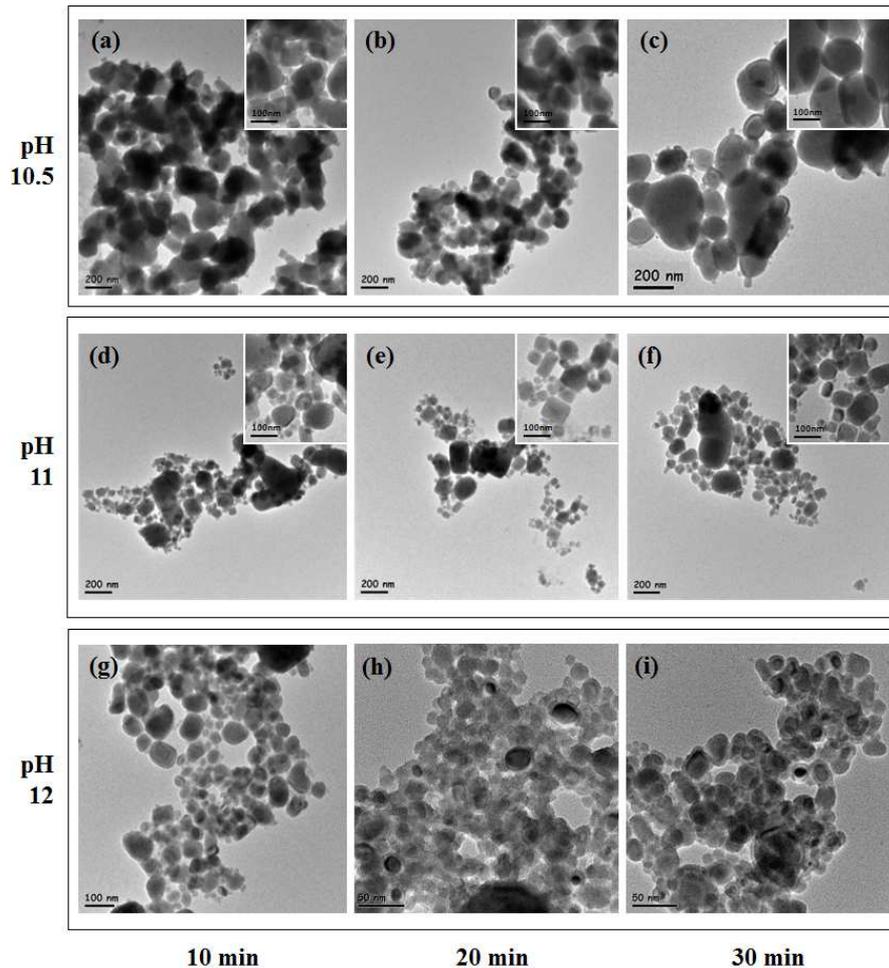


Fig. 3. TEM images of Sn NPs synthesized at different pH values. The reaction duration was set to 10 min, 20 min, and 30 min. The inset images were acquired at high magnification.

uniformity of the NPs. The size distribution of the NPs as a function of the reaction time and pH is summarised in Fig. 4. It can be observed that the increase in pH decreased the average size and size deviation of the synthesized Sn NPs. Thus, we assume that in the modified polyol synthesis of Sn NPs, an increase in pH accelerates the rate of reduction of Sn ions because of the higher activity of the reductant at higher pH, resulting in an increase in the number of nucleated particles [4]. The concurrent formation of many nuclei might simultaneously reduce the average particle size and enhance the size uniformity [5].

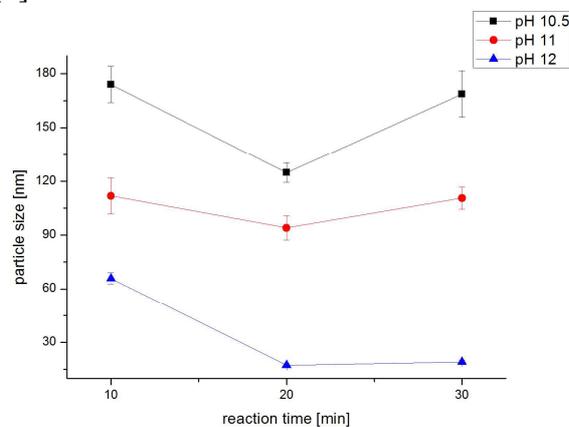


Fig. 4. Particle size distribution of Sn NPs synthesized at different pH values for various reaction durations.

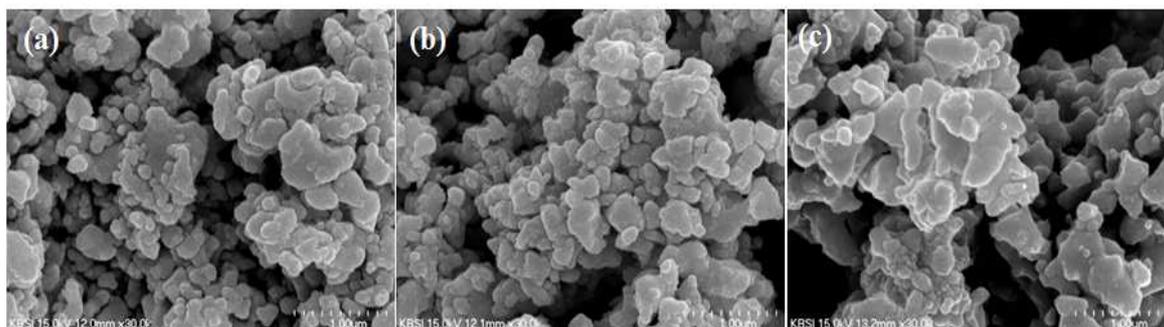


Fig. 5. SEM images of dried Sn NPs synthesized at pH values of (a) 10.5, (b) 11, and (c) 12.

SEM images of the Sn NPs dried after the synthesis are presented in Fig. 5. It can be observed that most of the particles appear aggregated. In addition, the average size of each particle was much larger than that measured in the TEM image. The large particles observed in the dried sample of NPs synthesized at pH 12 were equal in size to the desiccated particles synthesized at pH 10.5. Hence, excessive agglomeration and coagulation between the as-synthesized particles occurred during drying even at room temperature, which makes the differences among the sizes of the as-synthesized particles insignificant.

Summary

The effect of increasing pH (from 10.3 to 12) on the morphology and size distribution of Sn NPs synthesized using a modified polyol method was investigated. Unagglomerated Sn NPs could be successfully synthesized using the wet chemical process. When the pH value increased, the average size and size deviation of the synthesized Sn NPs decreased. As a result, the quality of the Sn NPs synthesized at pH 12 was the best. The increase in the pH value is believed to enhance the rate of reduction of Sn ions during the synthesis, resulting in an increase in the number of nucleated particles. The concurrent formation of many nuclei may have led to the reduction in the average particle size and enhancement in size uniformity. Observation of the particles dried at room temperature indicated the occurrence of excessive agglomeration and coagulation between the as-synthesized particles during the drying process, regardless of the size of the as-synthesized particles.

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