Optimization of electrolyte concentration and voltage for effective formation of Sn/SnO_2 nanoparticles by electrolysis in liquid

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Abstract

This work investigates the optimum experimental conditions required for the synthesis of Sn nanoparticles (Sn-NPs) via surfactant-free direct-current electrolysis using KCl as the electrolyte. Metallic Sn wire was used as a cathode, which was melted by the local concentration of current upon the application of a direct-current voltage. The effect of electrolyte concentration was analyzed by varying the concentration from 0.01 to 1.0 M, under constant electric power of 40 W. Results indicated that the applied voltage required for plasma generation increased with a decrease in the electrolyte concentration and the particle size decreased at high applied voltage with low electrolyte concentration; particles with a mean diameter of 258.5 nm formed at 0.05 M. However, coarse $Sn_6O_4(OH)_4$ crystals were precipitated at a concentration of 0.01 M. Therefore, the optimum concentration required for the formation of smaller particles was determined to be 0.05 M. Subsequently, the effect of voltage was analyzed by varying the applied voltage from 70 to 190 V. As a result, the effective production energy of 45 Wh/g was obtained at voltages ranging from 110 to 130 V.

Keywords

Sn nanoparticles, production energy, electrolysis, discharge, direct current

1. Introduction

Sn and Sn-based alloy nanoparticles are being widely used in lead-free solder paste[1, 2] and as anode materials in batteries[3, 4] owing to their low melting point and high surface area. Current Li-ion batteries, with graphite and other carbonaceous materials as standard anode materials, have a maximum theoretical capacity of 372 $mAh \cdot g^{-1}$, corresponding to the intercalation of Li_6C. Although this capacity is not considered very low, new anode materials with higher capacities than those available commercially are required to produce lightweight batteries with high energy density. Recently, Sn nanoparticles anodes have attracted much attention because of their high theoretical capacity of 992 $mAh \cdot g^{-1}$ to form a $Li_{4.4}Sn$ alloy.

Discharge electrolysis in an aqueous solution is a novel electrochemical process that has been recently used for the synthesis of various nanoparticles[5-7]. In addition, unconventional electrolysis methods, including plasma-induced cathodic discharge in a molten salt[8] and arc discharge in liquid[9], are being used for the synthesis of nanoparticles. In general, the synthesis of nanoparticles by electrolysis in liquid media offers many advantages such as (1) simplicity of the experimental setup, (2) higher productivity than conventional solution processes, and (3) feasibility for the synthesis of alloy nanoparticles[10]. In one of our previous studies reported elsewhere[11], we

demonstrated the synthesis of Sn nanoparticles (Sn-NPs) via electrolysis in K_2CO_3 solution. However, the Sn-NPs prepared in this study additionally contained colloidal SnO_2 particles [11, 12]. When alkaline solutions are used in the electrolysis process, Sn tends to react with the $(OH)^-$ ions in the solution to form $Sn(OH)_3^-$ ions, which further gets transformed to $Sn_6O_4(OH)_4$ and SnO_2 crystals. Besides, this process required the use of surfactants such as cetyltrimethylammonium bromide (CTAB) to prevent the ionization of Sn[12]. However, it is highly challenging to remove CTAB from the final product. Herein, we demonstrate a novel surfactant-free method for the synthesis of Sn-NPs via direct-current electrolysis in neutral KCl solution.

In our previous studies reported elsewhere[13, 14], we found that electrolyte concentration greatly affects the formation of nanoparticles. In the case of a nickel cathode, the voltage required for producing a discharge tends to decrease at high electrolyte concentrations, due to an increase in the electrical conductivity of the solution. Consequently, higher electrolyte concentration results in high current flow, which in turn leads to the formation of larger particles. This suggests that a lower electrolyte concentration is desired for the synthesis of smaller particles. Therefore, in this study we analyzed the optimum electrolyte concentration and voltage conditions

required to achieve smaller particle size, high purity, high yield, and highly energy efficient production of Sn-NPs.

2. Experimental

2.1. Experimental setup and procedure

Figure 1 (a) shows the schematic diagram of the experimental apparatus used for the synthesis of Sn-NPs. In the typical setup, 99.9 mass% pure Sn wire of diameter 2.0 mm, which was used as the cathode, was placed at the center of the glass cell. The anode consisted of a Pt wire of length 1000 mm and diameter 0.5 mm, bent in the form of a semicircular mesh. The electrolyte was composed of 300 ml of KCl solution with concentrations varied from 0.01 to 1.0 M. The voltage was fixed to a constant value for a time period of 1 h, during which the electric power W was kept at 40 W. When the effect of voltage was investigated, the applied voltage was varied from 70 to 190 V. During electrolysis, the solution was stirred using a magnetic stirrer at a rate of 600 rpm. The values of current, voltage and solution temperature were recorded every 2 s. Figure 1 (b) shows the experimental procedure adopted in this study for the synthesis of Sn-NPs. As the first step of the process, the weight of the electrode was measured. Subsequently, Sn-NPs were synthesized by applying appropriate voltage. Finally, after consumption of the electrode tip, the electrode weight was measured once again. This procedure was repeated until 0.5 g of Sn-NPs was obtained.

2.2. Product analysis

After the experiments, the products were collected by centrifugation. The collected particles were washed with deionized water to remove KCl. After drying, the particles were characterized using powder X-ray diffraction (XRD, Cu-Kα, Miniflex, Rigaku, Tokyo, Japan), scanning electron microscopy (SEM, JSM-7001FA, JEOL, Tokyo, Japan), and transmission electron microscopy (TEM, JEM-2010F, JEOL) microscope. Particle size analysis was performed using dynamic light scattering measurements (Nanotrac UPA-UT151, Microtrac, Inc., Tokyo, Japan).

Furthermore, we evaluated the production energy Q (W·h/g), which indicates the amount of energy required for the synthesis of Sn-NPs. The input power W (W·h) can be calculated from the recorded voltage and current, using the following equation:

$$\text{Power}, W(W \cdot h) = E(V) \int I(A)\, dt / 3600 \quad (1)$$

The amount of Sn-NPs M (g) synthesized in the process was measured by calculating the difference in the mass of the electrode wire before and after electrolysis. Accordingly, the production energy Q (W·h/g) was derived from W (W·h) and M (g), using the following relation:

$$\text{Production Energy}, Q(W \cdot h / g) = W(W \cdot h) / M(g) \quad (2)$$

3. Results and discussion

3.1. Effect of electrolyte concentration

Table I summarizes the applied voltages and the resulting current for different concentrations of the electrolyte. Similar to the trend observed in case of Ni electrode, the applied voltages for plasma formation decreased at higher concentrations of the electrolyte due to an increase in the electrical conductivity of the solution. Figure 2 shows the XRD patterns of the Sn samples synthesized under different concentrations of the electrolyte. As can be seen from the diffraction patterns, the samples synthesized with the electrolyte concentrations in the range of 0.05 to 1.0 M exhibited mixed Sn and SnO_2 phases. For the electrolyte concentration of 0.01 M, the XRD pattern indicated the formation of $Sn_6O_4(OH)_4$. Figure 3 shows the particle size distribution of the Sn-NPs prepared in this study. Results indicate that the particle size tends to decrease at high applied voltage with a low concentration of the electrolyte. At the electrolyte concentration of 0.01 M, the particle size was larger because of the formation of $Sn_6O_4(OH)_4$ crystals. Of all the different concentrations of the electrolyte used in this study, the smallest particle size of 258.5 nm was obtained at the concentration of 0.05 M.

Table I. Applied voltage and resulting current for different electrolyte concentrations.

Concentration (M)	0.01	0.05	0.1	0.5	1.0
Voltage (V)	200	170	140	100	80
Current (A)	0.20	0.25	0.30	0.42	0.50

Figure 4 shows the plot between the amount of Sn-NPs synthesized M (g) and the input power (Wh), for different concentrations of the electrolyte. As shown in the equation (2), the gradient of the linear line indicates the production energy (Wh/g). As can be seen from the plot, the electrolyte concentration of 0.1 M exhibits the lowest production energy of 51.1 (Wh/g). The electrolyte concentration of 0.05 M required the production energy of 65.9 (Wh/g). From these results, it can be concluded that the optimum electrolyte concentration is 0.05 M because of the smallest particle size.

The samples were further analyzed using SEM and TEM. As can be seen from the SEM images in Fig. 5, particles produced from 0.05 to 1.0 M were spherical, and the particle sizes decreased at lower concentrations. These particles were formed as a result of melting the Sn electrode surface. To clarify the location of the SnO_2, the prepared Sn-NPs were characterized using TEM. Figure 6(a) shows the bright-field TEM image

of the 0.05 M, 170 V products, and Figs. 6(b, c) show the selected area electron diffraction (SAED) patterns corresponding to the area indicated by the dotted line in Fig. 6 (a). From these SAED patterns, it is found that spherical Sn particles and colloidal SnO_2 particles were formed. These SnO_2 particles were probably produced as a result of the high-temperature atmosphere above the melting point surrounding the Sn electrode surface. On the other hand, at the electrolyte concentration of 0.01 M, octahedral crystals of $Sn_6O_4(OH)_4$ were probably precipitated, as described in the following equations.

$$Sn^{2+} + 3(OH)^- \rightarrow Sn(OH)_3^- \quad (3)$$

$$6Sn(OH)_3^- \rightarrow Sn_6O_4(OH)_4 + 4H_2O + 6(OH)^- \quad (4)$$

It is assumed that the higher accelerating voltage used in the electrolysis process led to the ionization of the Sn electrode, resulting in the formation of $Sn(OH)_3^-$ ions, as shown in Eq. (3). The $Sn(OH)_3^-$ ions in solution was further transformed to $Sn_6O_4(OH)_4$, as shown in Eq. (4).

3.2. Effect of applied voltage

We investigated the effects of applied voltage on the composition, production energy, and particle size of the sample at the fixed electrolyte concentration of 0.05 M. Figure 7 shows the XRD pattern of the samples obtained by varying the voltage from 70 to 190 V. In the high-voltage range of 170 to 190 V, the resulting Sn-NPs were partially oxidized to SnO_2. Figure 8 (a) shows average solution temperature during electrolysis, where the solution temperature increased with an increase of applied voltage. From this result, there is a possibility that particle oxidation was induced by the high solution temperature. At voltages below 150 V, the oxide phase was not observed, because of the decrease in solution temperature.

Figure 8 (b) shows the production energy and particle size of the samples obtained under different voltage conditions. As can be seen from the figure, effective production energy of around 45 (Wh/g) was obtained for voltage conditions ranging from 110 to 130 V. The value of 45 (Wh/g) indicates that the input power of 45 Wh is required for the synthesis of 1 g of Sn-NPs. At high voltages above 170 V, the temperature surrounding the Sn electrode exceeded too high, making it unsuitable for the effective synthesis of Sn-NPs. On the other hand, at voltages below 90 V, the production energy required for the process was high because of the lack of heat under low voltage

conditions. Furthermore, we evaluated the mean diameter of the samples obtained at different voltage conditions. As can be seen from Fig. 8 (b), the applied voltage of 190 V resulted in the formation of coarse particles with oxide phase due to the high-voltage conditions. For applied voltages below 170 V, the resulting particle size increased with a decrease in the production energy. When the production energy was low, large amount of particles were generated. Consequently, the particles tend to agglomerate and result in larger particle size.

4. Conclusions

In summary, we have investigated the effects of electrolyte concentration and voltage on the formation of Sn-NPs by direct-current electrolysis in neutral KCl solution. The composition, morphology, particle size, and production energy of the Sn-NPs were analyzed and the conclusions are summarized as follows.

(1) The particle size of Sn-NPs decreased at high applied voltage with a low concentration of the electrolyte. The optimum concentration required for the formation of small Sn particles was determined to be 0.05 M.

(2) The KCl concentration of 0.01 M did not result in the formation of Sn-NPs due to the ionization of Sn under high-voltage conditions.

(3) At the optimum concentration of 0.05 M, effective production energy of 45 Wh/g was obtained for the applied voltages ranging from 110 to 130 V. Higher voltages over 170 V induced the oxidation of the particles.

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Figure Captions

Figure 1 (a) Schematic diagram of the experimental setup used for the synthesis of Sn-NPs. Sn wire was used as the cathode. During electrolysis, the KCl solution with different concentrations was stirred using a magnetic stirrer at a rate of 600 rpm. (b) Experimental procedure adopted for the synthesis of Sn-NPs. As the first step, the weight of the electrode was measured. Subsequently, Sn-NPs were synthesized by applying voltage. Finally, after the consumption of the electrode tip, the electrode weight was measured once again. This procedure was repeated until the synthesis of 0.5 g of Sn-NPs.

Figure 2 XRD patterns of the products synthesized at different KCl concentrations of the electrolyte. From 0.05 to 1.0 M of KCl, Sn and SnO_2 phases were formed. In contrast, the 0.01 M concentration of KCl, the $Sn_6O_4(OH)_4$ were synthesized.

Figure 3 particle size distributions of the products at different electrolyte concentrations. Particle sizes were measured by dynamic light scattering. The particle size was decreased with decreasing the electrolyte concentrations. At 0.01 M, particle size was big because of the $Sn_6O_4(OH)_4$ crystals formation.

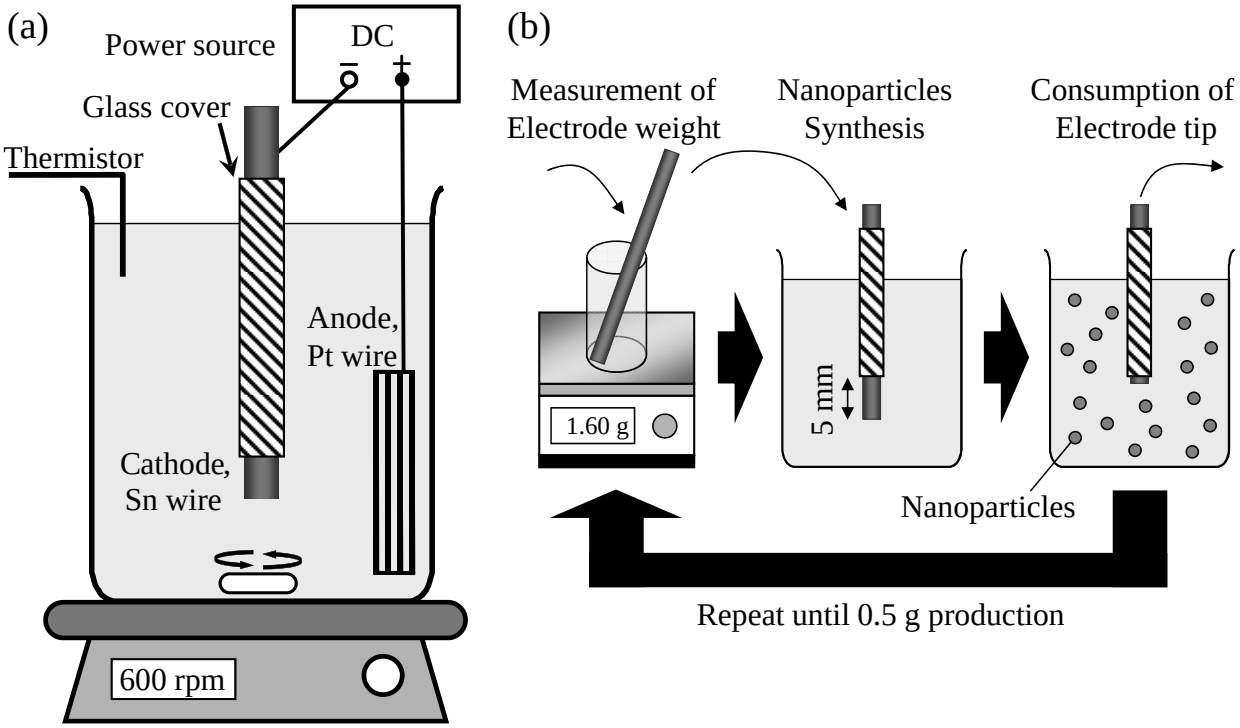
Figure 4 Plot between the amount of Sn-NPs synthesized in the process M (g) and the input power (Wh). The gradient of linear line indicates the production energy (Wh/g). The KCl concentration of 0.1 M required the lowest production energy.

Figure 5 SEM images of the products at different electrolyte concentrations of (a) 1.0 M, (b) 0.1 M, (c) 0.05 M, and (d) 0.01 M. Particles produced from 0.05 to 1.0 M were spherical, in which the particle size decreased at lower concentration. In contrast, at the 0.01 M concentration, the octahedral shapes were precipitated.

Figure 6 TEM images of the 0.05 M, 170 V products: (a) bright-field TEM image, and (b, c) electron diffraction patterns from (a).

Figure 7 XRD patterns of the products synthesized at different voltages with the electrolyte concentration of 0.05M. When the voltage was over 170V, the tin oxide was formed due to the high tempeature surrounding the electrode.

Figure 8 (a) Average solution temperature during electrolysis. (b) The amount of Sn-NPs synthesized in the process M (g) plotted as a function of the input power (Wh) and mean particle diameter (μm). The voltages ranging from 110 to 130 V are considered to be suitable for the effective production of Sn-NPs.



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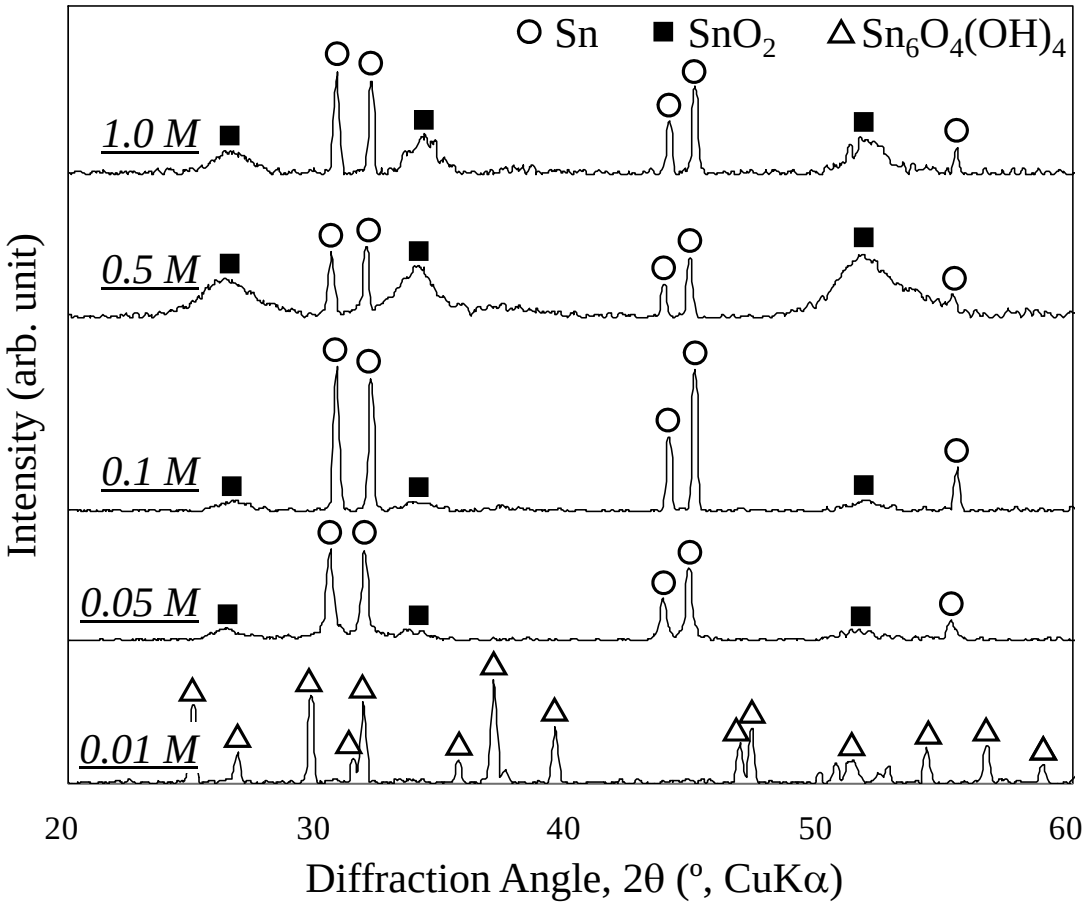

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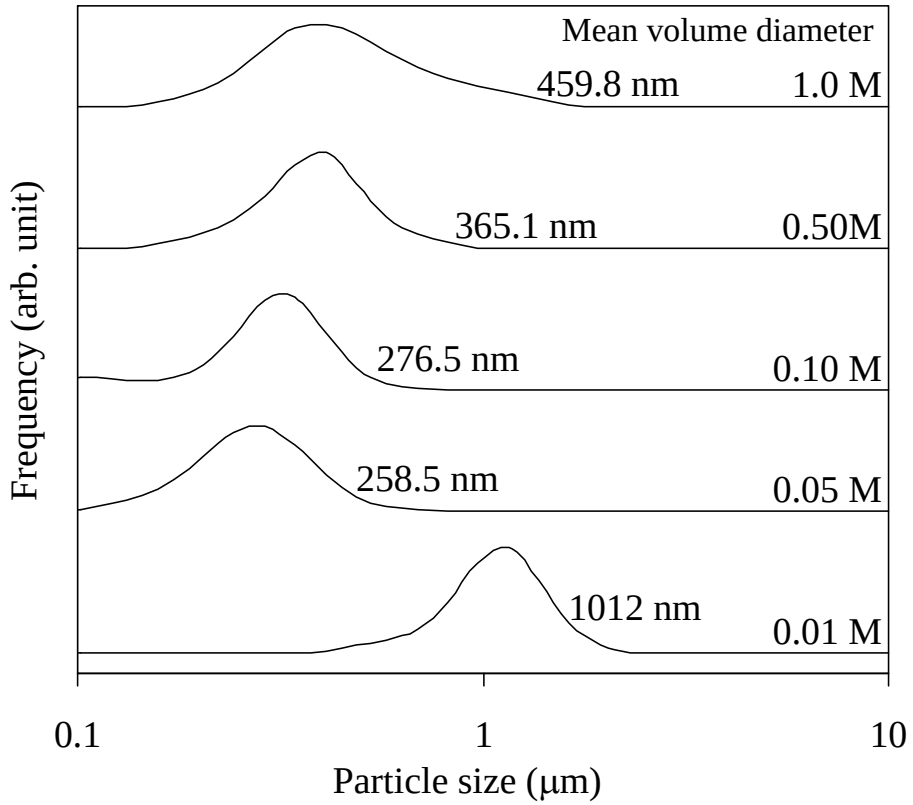

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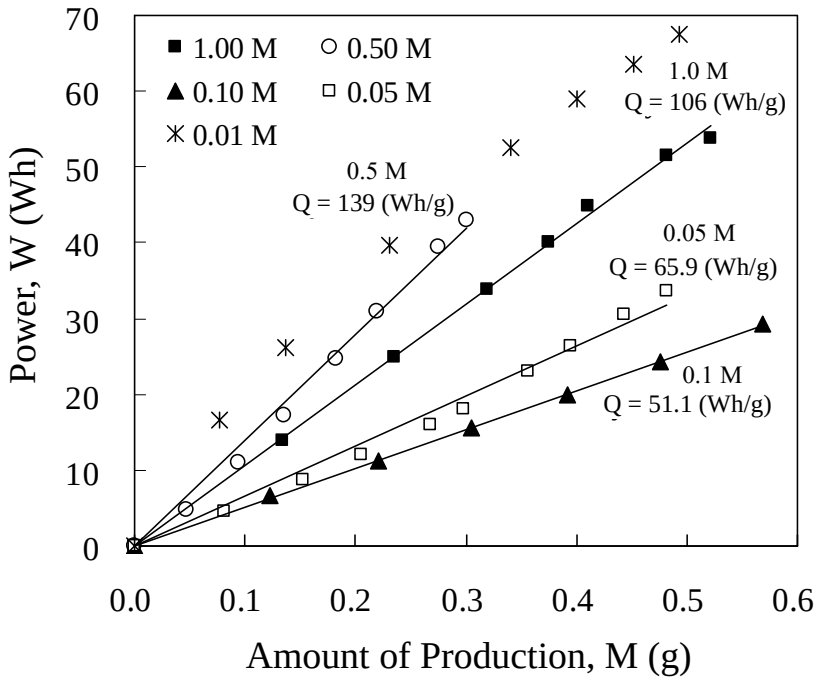

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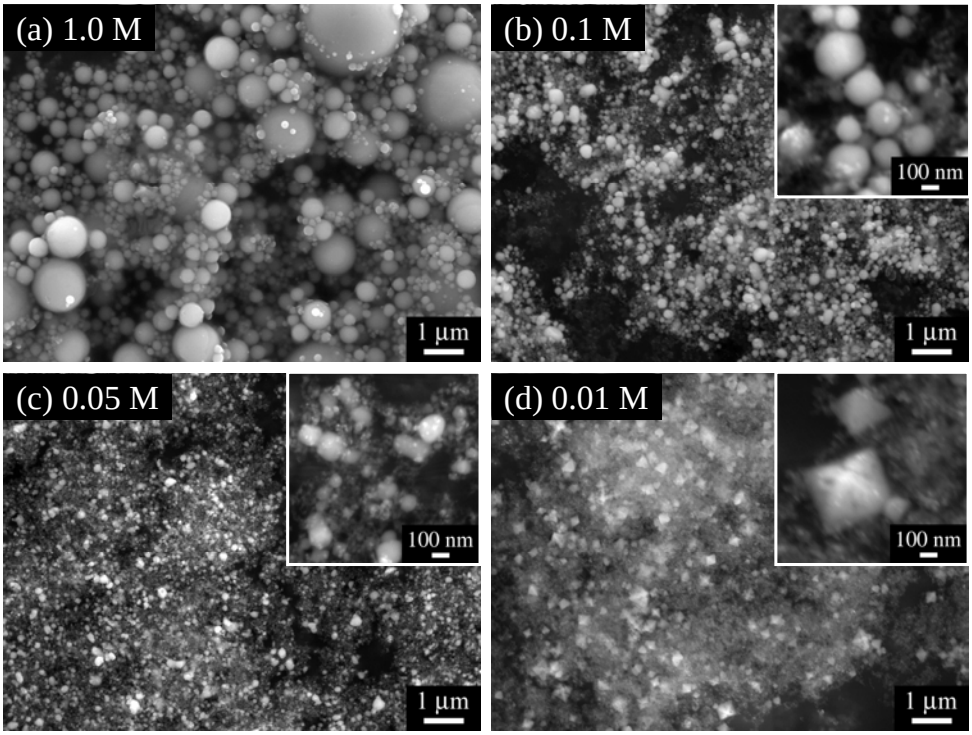

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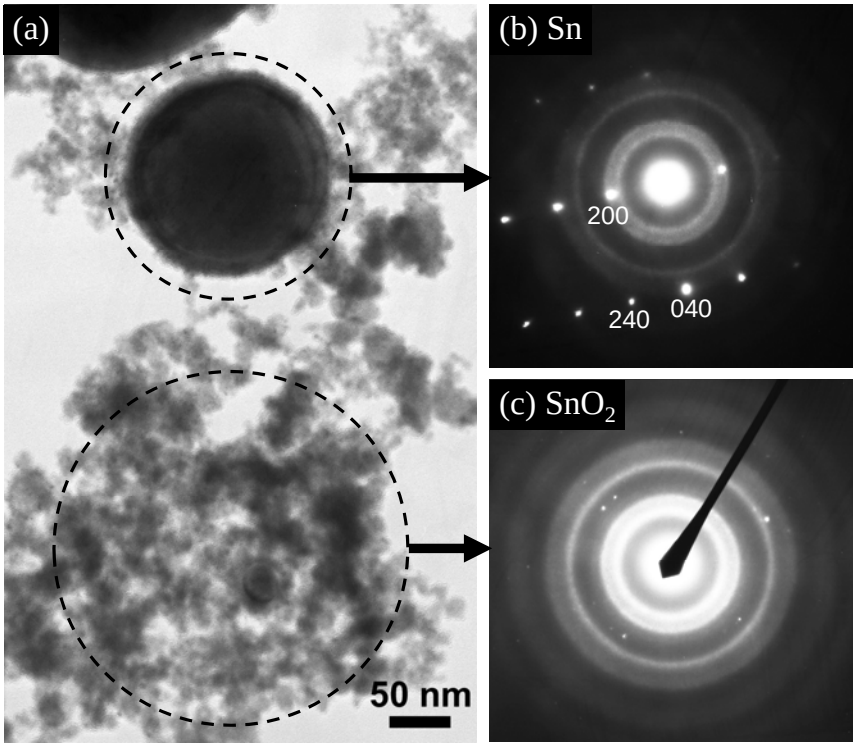

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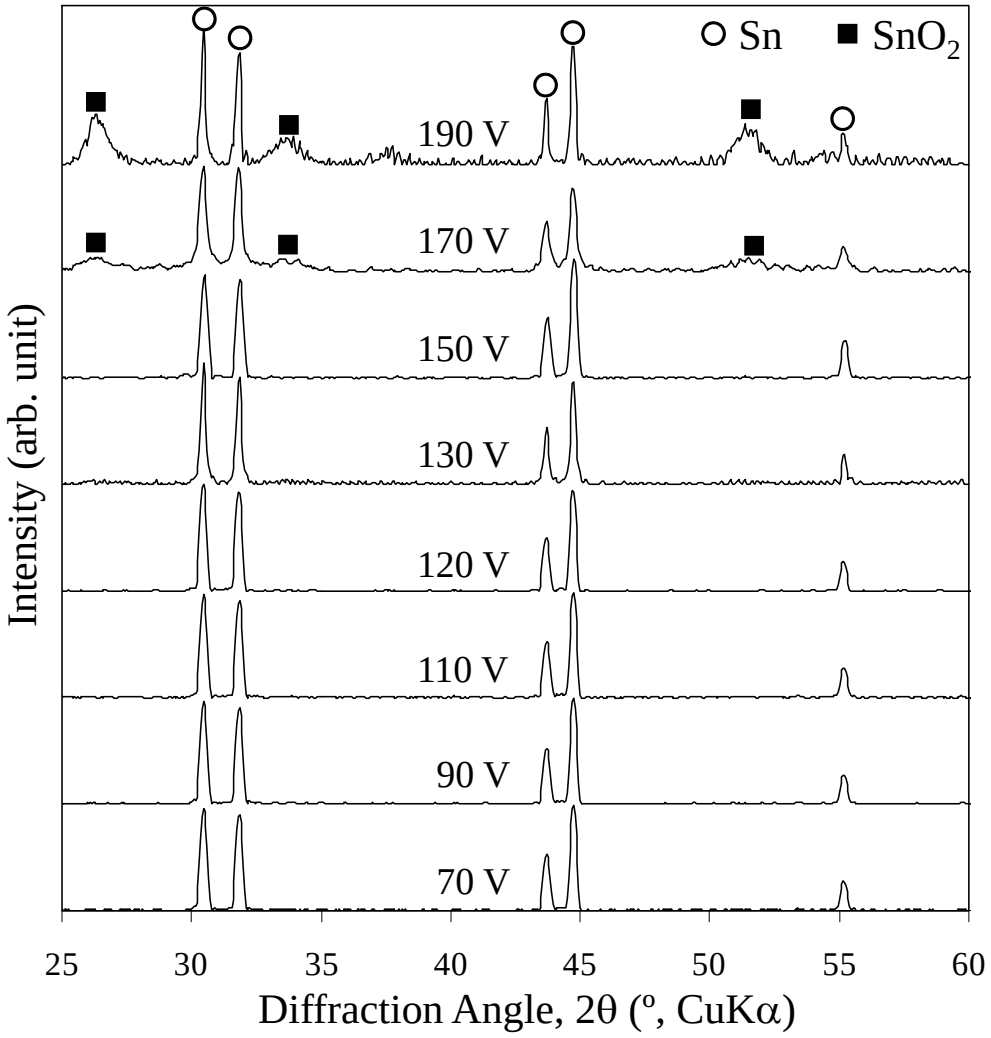

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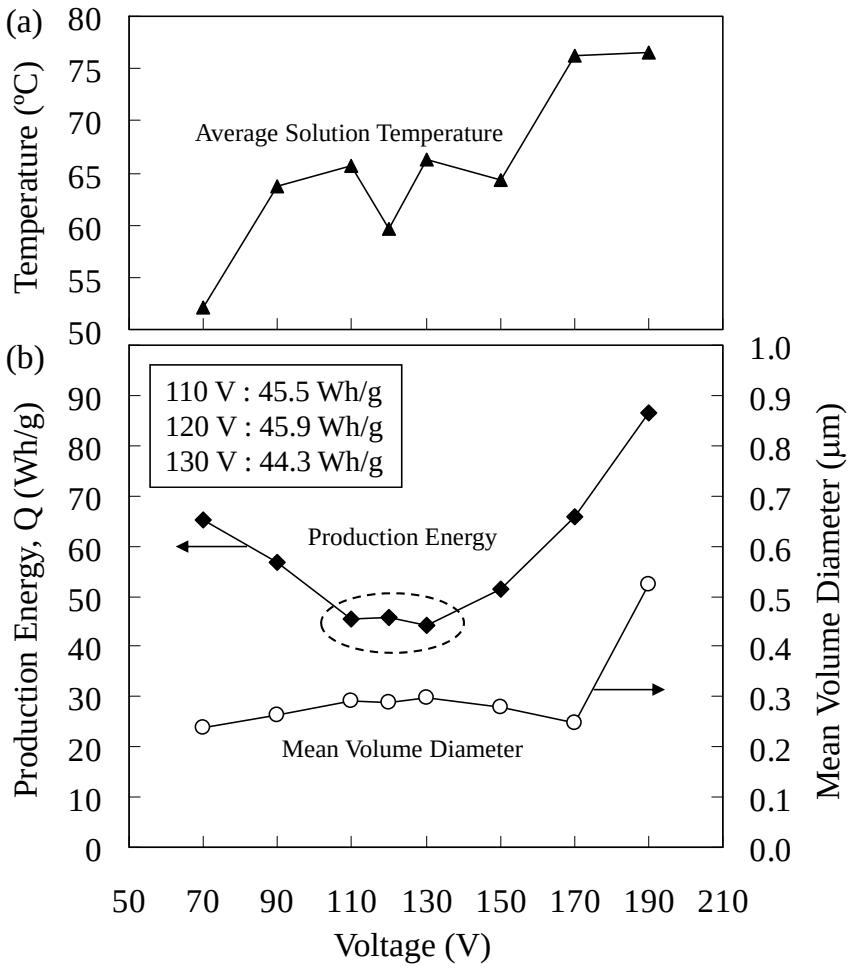

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