Hot-Injection Thermolysis of Cobalt Antimony Nanoparticles with Co(II)-Oleate and Sb(III)-Oleate

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ABSTRACT

A novel strategy for the synthesis of CoSb_2 nanoparticles is demonstrated via preparation of novel organometallic complexes. Hydrated cobalt oleate (CoOl) and non-hydrated antimony oleate (SbOl) complexes are synthesized as precursors. The CoSb_2 nanoparticles are prepared by hot injection, which involves thermolysis of CoOl and SbOl in a non-coordinating solvent at 320°C . The coordination modes and distinct thermal behaviors of the intermediate non-hydrated SbOl complexes are comparatively investigated by thermo-analytical techniques. When the reaction temperature is increased, the particle size is found to increase linearly. The crystallinity of the CoSb_2 nanoparticles prepared at 250°C is amorphous phase without any peaks. CoSb_2 structural peaks start to appear at 300°C and dominant peaks with high crystallinity are synthesized at 320°C . The potential chemical structures of non-hydrated SbOl and their reaction mechanisms by thermolysis are elucidated. The elemental composition and crystallographic structure of CoSb_2 nanoparticles suggest a bimodal interaction of the organic shell and the nanoparticle surface, with a chemical absorbed inner layer and physically absorbed outer layer of carboxylic acid.

Key words : Solution process, Coordinate, CoSb_2 nanoparticles, Thermolysis, Hot-injection

1. Introduction

Due to their high energy density and long cycle life, Li-ion batteries are used to power portable electronic devices, ranging from small-scale electronic devices to electric vehicles. On the one hand, there is a substantial interest in increasing the energy density of Li-ion batteries; on the other hand, there is a growing need for battery flexibility and shape adaptation in order to meet consumer needs and demands.^{1,2)} Among all battery technologies, Li-ion batteries exceed any rival technology by at least a factor 2.5 in terms of energy density.³⁾ However, the use of Li-ion batteries in emerging PHEVs (plug-in hybrid electric vehicles), HEVs (hybrid electric vehicles) and EVs (electric vehicles) requires further improvements in such areas as energy density, cycle life, environmental compatibility and safety. To resolve these problems, large efforts have been made to develop innovative electrode materials with specifically engineered nanostructures.⁴⁾ Especially, nanocrystalline alloys are interesting candidates as anode materials in lithium-ion batteries because, due to their smaller particle size and

larger specific surface area, these alloys have more attractive properties than those of micro-sized alloy particles. The use of nanosized particles could improve the kinetics of Li-ions diffusion and result in an improvement of the electrochemical performances of electrodes.⁵⁾ Nanocrystalline CoSb_2 nanoparticles could be used as a potential anode material in lithium-ion batteries. It was reported that electrodes fabricated with CoSb_2 nanoparticles exhibited large reversible capacity with good cycling behavior. Nanosized alloy particles with excellent electrochemical performance are a strong candidate as a promising anode material in lithium-ion batteries.⁶⁾

The synthesis of metal oxides and metal nanoparticles by the thermolysis of a metal oleate (MeOl) complex has received significant attention compared to conventional methods such as hydrothermal and oil phase syntheses.⁷⁾ Hyeon et al. report on the nucleation kinetics of iron oxide nanocrystals during thermolysis of the FeOl complex in a high boiling point solvent.⁸⁾ Also, cobalt ferrite nanoparticles with a narrow size distribution have been synthesized by thermolysis of the Fe-CoOl complex. The influence of aging time during the decomposition of the Fe-CoOl complex has been studied in terms of the structure, chemical composition, size, and magnetic relaxation of cobalt ferrite nanoparticles.⁹⁾ Uniform sphere-like Co-doped iron oxide nanoparticles have also been studied in the thermolysis of FeOl and CoOl

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in the presence of oleic acid (OA). The particle size of co-doped iron oxide can be changed by variation of the Co/Fe mole ratio.¹⁰ In this work, nearly monodisperse, strongly crystalline, superparamagnetic CoFe_2O_4 nanoparticles with diameters of 6 nm can be synthesized in an OA-water-pentanol system. Another approach, i.e. hydrothermal synthesis, is used as an efficient and eco-friendly alternative method. The particles are synthesized by changing the reaction conditions such as the hydrolysis of MeOl in organic phase. Particle size of 5-8 nm diameter can be tuned by polarity-driven precipitation into the water phase.¹¹ It is also possible to prepare CoO nanocrystals (CoO NCs) by thermolysis of CoOl complex. Fatty acid coated nanoparticles are transferred to the water phase via facile phase-transfer method with amphiphilic surfactants such as anionic (sodium dodecyl sulfate, SDS), neutral (Pluronic F127, PF127) and cationic (cetyltrimethyl ammonium bromide, CTAB) surfactants.¹² Clavel *et al.*¹³ report cobalt and manganese doped ZnO achieved using the solvothermal method, which involves the reaction of zinc and cobalt acetate or MnOl in benzyl alcohol and which leads to pure inorganic nanoparticles. The addition of an inert solvent, which is used to control the amount of benzyl alcohol, drastically influences the particle morphologies, which strongly influence the magnetic behavior.

The size and shape of the cobalt particles can be controlled by the interface between the particles and the adsorbed species.¹⁴ Polymeric matrixes are used as stabilizing agents to restrict the nucleation; these matrixes are replaced by metal coordinating agents such as OA.¹⁵ Remarkably, metastable ϵ -cobalt phase can be prepared in the presence of TOPO or TPP, resulting in a crystal symmetry like that in β -manganese.¹⁶ Schällibaum *et al.*¹⁵ report ϵ -cobalt nanoparticles with an average diameter of 4.5 nm fabricated by controlling the experimental conditions with larger quantities; process was based on thermal decomposition of dicobaltoctacarbonyl in the presence of OA and trioctylphosphine oxide (TOPO).

Xie *et al.*^{17,18} report nanocrystalline CoSb_2 obtained using solvothermal method at various temperatures. However, a sample prepared at 190°C retained unreacted Sb. Amornpitoksuk *et al.*¹⁹ reported nanocrystalline CoSb_2 formed by mechanical alloying with elemental Co and Sb powder. An arsenopyrite structure of CoSb_2 starts to appear after 30 h of mechanical milling, with low crystallinity. Compared to these results, the thermolysis of hydrated CoOl and non-hydrated SbOl in non-coordinating solvent at 320°C shows high crystallinity of CoSb_2 without any impurity phases.

In this work, we use a novel method to prepare organometallic precursors for thermal decomposition. When Sb is contact with water/moisture, it undergoes hydrolysis, forming antimony oxychloride and releasing hydrogen chloride, thus it is impossible to use Sb to prepare SbOl via conventional ion exchange with NaOl. To avoid hydrolysis, antimony trichloride is used to directly coordinate equimolar of metal ions with OA, resulting in non-hydrated SbOl. In contrast, CoOl prepared by direct coordination of metal ions with carboxylic acid shows very poor yield and synthetic properties. Consequently, CoOl is prepared by ion exchange with NaOl, resulting in hydrated CoOl. Eventually, the hot-injection method is used to overcome the different decomposition temperatures of the non-hydrated SbOl and hydrated CoOl. The particle sizes of CoSb_2 synthesized by thermolysis of metal oleate can be tuned by changing the reaction time and temperature.

2. Experimental Procedure

Cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), antimony chloride (SbCl_3), oleic acid (OA, 90.0%), hexane (99.0%), ethanol (95%) and 1-octadecene (ODE, 90.0%) were obtained from Sigma-Aldrich. Sodium oleate (NaOl , $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COONa}$) was supplied by Junsei Chemical. All the chemicals except ODE were used without further purification. Volatile substances such as absorbed water and organic impurities with a low Mw in ODE were evaporated by heating at 200°C for 3 h prior to use. Double distilled and deionized water was used throughout. Hydrated CoOl complexes were produced by Hyeon's method⁸) by directly reacting cobalt(II) chloride and NaOl. Briefly, 4.758 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 12.178 g of NaOl were dissolved in a mixture solvent composed of 80 mL EtOH, 60 mL distilled water and 140 mL hexane in a closed bottle. The resulting solution was heated to 70°C and kept at that temperature for 4 h. When the reaction was complete, the upper organic layer containing the CoOl complex was washed three times with 30 mL distilled water in a separatory funnel. After washing, hexane was evaporated off, resulting in the CoOl complex being in a waxy solid form. SbOl was prepared using the previously reported method¹⁰) by directly coordinating the antimony chloride and OA (Table 1) in a three-neck round-bottom flask. The mixture was heated to 120°C to remove the physically absorbed water and the by-product, HNO_3 . During the reaction, the mixture color changed to brownish from transparent. The temperature of the reactants was decreased to room temperature and reactants

Table 1. Sample Notation and Composition of CoOl and SbOl

Sample notation	Metal source (C, A)	Surfactant (S, O)	Solvent (M, N)
CoOl-CSM	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	Na Oleate	Mixture of hexane, EtOH and water
SbOl-AONx (x = 2,3,4)	SbCl_3	Oleic acid	None

In sample notation, "C" means cobalt chloride, "A" means antimony chloride, "S" means sodium oleate, "O" means oleic acid, "M" means mixture of solvents, "N" means direct reaction without solvent

were collected for analysis. The sample notation and preparation methods are described in Table 1. For example, 2 mmol (1.244 g) CoOI was dissolved in 35 mL of ODE in the three-neck round-bottom flask, degassed in a vacuum, purged three times with argon, and heated to 250, 300 and 320°C. The holding time was varied from 10 to 60 min. At these temperature, the solution of SbOI in 5 mL of ODE was quickly injected into the reaction vessel under magnetic stirring and the color of the solution changed immediately from light blue to dark black, indicating that the nucleation and subsequent growth of CoSb₂ Nanoparticles had occurred. After the desired holding time, the mixture was cooled to room temperature. The lipid-coated CoSb₂ Scheme 1 was dissolved in 5 mL hexane, precipitated by 10 mL ethanol and centrifuged at 14,000 rpm for 10 min; next, the supernatant was carefully decanted. The washing process was repeated 5 times and the lipophilic CoSb₂ nanoparticles were re-dispersed in 5 mL hexane, forming a stable suspension that was kept at 40°C for further use for characterization and application. Fourier transform infrared (FTIR) spectra were recorded at 20°C using ALPHA FT-IR spectrometers equipped with Platinum ATR (single reflection diamond ATR) from Bruker optics. The spectra were measured with a resolution of 1 cm⁻¹; the wavenumber range was 800 - 1,800 cm⁻¹. The samples were measured by dropping the samples on the surface of a facet of diamond ATR without any specific preparation of the specimens. Thermal gravimetric analysis (TGA), and differential thermal analysis (DTA) were carried out using a DTG-60H simultaneous DTA-TGA system from Micromeritics; differential scanning calorimetry (DSC) was performed using a DSC 50 from Shimadzu. In the data plots, the weight loss is expressed as a percentage of the initial sample weight and is plotted vs. temperature. DSC and DTA with nitrogen purge gas (20 mL/min) were used to heat samples (5-10 mg) in platinum pans with pierced lids (Micromeritics). Samples were measured from 20 to 400°C at a nominal heating rate of 10°C / min. X-Ray Diffraction (XRD) was measured using a D/max 2200V/PC from Rigaku. Samples were measured from 10 to 80° with a scan speed of 5 °/min. X-ray Photoelectron Spectroscopy (XPS) was performed using a PHI 5000 VersaProbe™ from Ulvac. Particle size was calculated using FWHM (Full Width at Half Max) and Scherrer's formula,²⁰⁾

$$t = (K \times \lambda) / (B \times \cos \theta B) \quad (1)$$

(*t* = thickness of crystallite, *K* = constant dependent on crystallite shape (0.89), *λ* = x-ray wavelength, *B* = FWHM or integral breadth, *θB* = Bragg angle).

3. Results and Discussion

In our synthesis strategy, CoSb₂ nanoparticles are synthesized by "hot-injection" method in which non-hydrated SbOI dissolved in ODE is directly injected into a hot solution of hydrated CoOI in ODE at a given temperature. In a binary reaction system, two metallic oleates are involved in the

reaction. Thus, the physiochemical properties of the metal oleate related to the two elements should be considered in order to nucleate the CoSb₂ nanoparticles. Especially, because the reaction activities of the hydrated CoOI and the non-hydrated SbOI precursors differ from each other, a separated nucleus will be generated and grow into a heterogeneous structure. A hydrated CoOI complex was advantageously prepared⁸⁾ by coordination of divalent inorganic salts and carboxylic acid (RCOOH) with various molar ratios at 120°C. The divalent metal ion can be introduced in any of a variety of forms, but in particular a divalent inorganic metal salt is introduced. These multivalent transition metal cations and particularly Co(II) are essentially capable of coordination of RCOOH, including those that have 10 to 22 carbon atoms. Due to their strong metal cation chelating ability, carboxyl acid groups in monobasic carboxylic acid are ionized by neutralization with metal ions. Typical reaction equations for hydrated CoOI and non-hydrate SbOI complexes are described as follows:

Non-hydrated CoOI as an organometallic precursor is less suitable than hydrated CoOI for the synthesis of CoSb₂ by thermolysis. The particle sizes of CoSb₂ are tuned using equimolar ratios of metal ions and carboxylic acid, without excessive passivating surfactant/solvent. Especially, the molecular structures of non-hydrated SbOI complexes are strongly correlated to the molar ratio of Sb/OA, and the correlation of coordination modes; the thermal behavior of non-hydrated SbOI and their particle formation are investigated.

The molecular structures and thermal behaviors of non-hydrated SbOI and hydrated CoOI complexes were determined by FTIR, DSC, TGA and DTA. The solid waxy forms of non-hydrated SbOI and hydrated CoOI complexes were subjected to thermal analysis to study the reaction mechanism of nanoparticle formation. Based on FTIR data, non-hydrated SbOI samples can be seen to be a mixture of OA and SbOI with different coordination modes. Fig. 1(a) shows DTA curves of hydrated CoOI prepared by ion exchange with NaOI and non-hydrate SbOI prepared with a different molar ratio of antimony ion and OA. The first transition peak that appeared at 73°C for hydrated CoOI-CSM is due to the removal of EtOH, which was used as an immiscible solvent between the aqueous and oil phases for ion exchange of Na⁺ to Co²⁺. According to Bronstein, the second transition appears at 131°C for the crude hydrated CoOI-CSM sample due to the removal of chemically absorbed water,²¹⁾ whereas no such endothermic peak appeared for non-hydrated SbOI. The absence of this endothermic peak is supplementary evidence supporting the prediction of the

Fig. 1. (a) DTA curves and (b) TGA and DSC curves of hydrated CoOI prepared by exchanging the cobalt ion with NaOI and non-hydrate SbOI prepared with different molar ratio of antimony ion and oleic acid. (SbOI-AON2 ~ SbOI-AON4 and CoOI-CSM).

FTIR as can be seen in Fig. 1(a), the first endothermic peak of the non-hydrated SbOI complexes appeared at 262 - 276°C in all samples; this peak is assigned to the start of the dissociation of the oleate ligand. With an increasing ratio of OA against antimony ions, the endothermic peak was right shifted, indicating a stronger association of oleate ligand and antimony ion. The TGA curves show good agreement with the endothermic peak in Fig. 1(b). In non-hydrated SbOI-AON4 complexes, for example, the on-set temperature of the first weight loss is determined to be 215°C the weight loss from 215°C to 304°C is 49%.

The first transition appears at around 302 - 316°C in the DSC curves of the SbOI samples as a shallow exothermic peak. According to Bronstein and Hyeon^{8,21)} the peak near 300°C can be assigned to dissociation of the remaining oleate ligands from the hydrated metal oleate precursors that led to particle growth. Interestingly, the thermal decomposition temperature of OA was determined to be 266°C so, obviously, coordination with the metal ion had stabilized the oleate molecules and increased the decomposition/dissociation temperature of OA. In the non-hydrated

Fig. 2. FTIR spectra of oleic acid, hydrated CoOI prepared by exchanging the cobalt ion with NaOI and non-hydrate SbOI prepared with different molar ratio of antimony ion and oleic acid. (SbOI-AON2 ~ SbOI-AON4 and CoOI-CSM).

SbOI complexes, the amount of OA is increased from SbOI-AON2 to SbOI-AON4, which matches the fact that the endothermic transition peaks increased from 262°C to 276°C. The exothermic transition peaks match the second step weight loss from 296°C to 308°C, as can be seen in the TGA curve of SbOI-AON4 in Fig. 1(b). The weight loss of the second step is 39%, and thus it is reasonable to conclude that the first weight loss is due to the removal of free OA and the dissociation of one oleate ligand; the second weight loss from 276°C to 348°C is due to the dissociation of the remaining two oleate ligands. The significant separation of the transition peak of CoOI-CSM at 190°C is a clear indication of the complete separation of the nucleation and particle growth phases.

The structural influences of different amounts of OA are investigated for the formation of non-hydrated SbOI complexes and hydrated CoOI. Fig. 2 shows FTIR spectra of non-hydrated SbOI complexes prepared by varying the molar ratio

Scheme 1. Illustration of the CoSb_2 nanoparticles prepared by thermal decomposition of hydrated CoOl and non-hydrated SbOl complexes.

of SbCl_3 to OA from 1/2 to 1/4. Compared to pure OA, several new peaks appear in the region of $1,650 - 1,500 \text{ cm}^{-1}$ in all non-hydrated SbOl samples due to newly formed antimony carboxylate; also, a peak appearing at $1,435 \text{ cm}^{-1}$ is also assigned to carboxylate vibration. $1,558, 1,539$ and $1,517 \text{ cm}^{-1}$ are assigned to the $\nu_a(\text{COO})$ of the non-hydrated SbOl complexes, among which the band at $1,558 \text{ cm}^{-1}$ has the strongest intensity. A very small peak at $1,654 \text{ cm}^{-1}$ appeared in the SbOl-AON4 , and can be assigned to $\text{C}=\text{C}$ stretching mode, indicating that the double bond structure is intact in non-hydrated SbOl complexes. However, in SbOl-AON2 and SbOl-AON3 , this peak was too weak to detect. The intensity of the characteristic unreacted OA band at $1,698 \text{ cm}^{-1}$ increased with the decreasing ratio of SbCl_3 and OA, with SbOl-AON4 displaying the strongest intensity of $1,702 \text{ cm}^{-1}$ band, which could be explained by the increasing amount of solid dimerized unreacted OA. The distinguished peaks appeared at $1,435 \text{ cm}^{-1}$, and can be assigned to asymmetrical carboxylate vibration, indicating that bridging mode exists in these SbOl complexes. With increased OA concentration in the SbOl complex preparation, additional asymmetrical carboxylate vibration bands appeared at $1,517 \text{ cm}^{-1}$, resulting in a new $\Delta = 81 \text{ cm}^{-1}$ therefore, in the carboxylate the head binds to the antimony atom in both bidentate and bridging modes. In Bronstein's work, in the region of $1,600 - 1,500 \text{ cm}^{-1}$, several new peaks were identified as metal carboxylate bands; three bands at $1,558, 1,539$ and $1,517 \text{ cm}^{-1}$ were assigned to asymmetrical carboxylate vibration, whereas the strong band appearing at $1,435 \text{ cm}^{-1}$ was assigned to symmetrical vibration. In Fig. 4, a major peak can be seen to have appeared at $1,702 \text{ cm}^{-1}$; this peak can be assigned to the $\text{C}=\text{O}$ stretching band of OA or to asymmetrical vibration of unidentate mode.²²⁾ The intensities of the bands between $1,698$ and $1,702 \text{ cm}^{-1}$ increase linearly and shift wavenumber with the amount of OA increase. The coordination modes of the SbOl complexes were determined based on the position and separation of the asymmetrical and symmetrical antimony carboxylate peaks, and the splitting amount, Δ . Four types of metal carboxylate coordination modes are described in Scheme 2 ionic, unidentate, bidentate and bridging mode. For $\Delta > 200 \text{ cm}^{-1}$, the unidentate mode can be expected; for $110 \text{ cm}^{-1} < \Delta < 200 \text{ cm}^{-1}$, it is

* The other two valent is not shown in the scheme for simplicity

Scheme 2. Four coordination modes of antimony carboxylate: ionic, unidentate, bidentate and bridging.

the bridging mode; and for $\Delta < 110 \text{ cm}^{-1}$, it is the bidentate mode. The difference between characteristic bands within the $\nu(\text{COO-})$ region is 81 cm^{-1} , revealing the bidentate mode. In the case of CoOl , asymmetrical carboxylate vibration peaks at $1,406$ and $1,558 \text{ cm}^{-1}$ increased dramatically.

Figure 3 shows SEM images of the Co-Sb nanoparticles prepared by thermolysis of SbOl-AON3 and CoOl-CSM . a) the temperature of CoOl-CSM in ODE was found to increase to 320°C and SbOl-AON3 was hot-injected into ODE while holding the temperature for 10 min b) the temperature of SbOl-AON3 and CoOl-CSM in ODE was increased to 320°C while holding the temperature for 10 min. The hot injection method shows a size dispersion of the

Fig. 3. SEM images of CoSb_2 nanoparticles prepared by thermolysis of SbOl-AON3 and CoOl-CSM . a) the temperature of CoOl-CSM in ODE was increased to 320°C and SbOl-AON3 was hot-injected into ODE while holding the temperature for 10 min, and b) the temperature of SbOl-AON3 and CoOl-CSM in ODE was found to increase to 320°C and holding for 10 min.

CoSb nanoparticles that is remarkably small later adaptations have led to even smaller size dispersions than those that can be obtained using the conventional nucleation method. Nucleation and further crystal growth occur in different time stages. Especially, when mixtures of two organometallic compounds have different decomposition times and temperatures, nucleation is initiated from the substances with low decomposition temperature; further growth of another substance on the surface of the nuclei is formed as a separated phase. From Fig. 3(b), which shows a clear difference of the shapes, it can be seen that there are at least two different crystal structures. Antimony is quite volatile and starts to nucleate at a lower temperature than cobalt does. In contrast, it is difficult to nucleate cobalt at a lower temperature. Therefore, antimony particles were used as nuclei of the CoSb₂ particles and can be seen as plate-like shapes with a size of several micrometers; the CoOl was not intensively involved in further growth of the nuclei, which led to the round shaped particles. When an antimony precursor is injected into a hot solvent, antimony atoms start to coalesce simultaneously with cobalt atoms until a critical concentration is reached at which the metal atoms rapidly form small clusters. These clusters subsequently grow by diffusion, which is believed to proceed under conditions commonly applied during the metal precursor compound injection period.¹⁵⁾ A monomer precursor of metal oleates can combine to form small, unstable clusters of increasing free energy. In the case of the hot injection method, the free energy of formation of the CoSb₂ particles clusters with very small size distribution and increases with the growth of size until a maximum is reached. Based on these results, further experiments were performed using the hot-injection method.

The structure of the CoSb₂ nanoparticles prepared by thermolysis of SbOl-AON3 and CoOl-CSM was analyzed by XRD. Peaks were rather broad, indicating the nanocrystalline character of the as-synthesized CoSb₂ nanoparticles. Fig. 4(a) the temperature of CoOl-CSM in ODE was increased to 320°C and SbOl-AON3 was hot-injected into ODE while holding the temperature at 10 min for the conventional heating method. It was found that the temperature of SbOl-AON3 and CoOl-CSM in ODE increased to 320°C temperature was held for 10 min. The major diffraction pattern agrees well with the monoclinic arsenopyrite structure of CoSb₂ (space group P21/c). Both hot injection and the conventional method show a single phase without an impurity phase.

Figure 5 shows SEM images of CoSb₂ nanoparticles prepared by thermolysis of SbOl-AON3 and CoOl-CSM at different reaction temperatures. The reaction temperature of CoOl-CSM in ODE was increased to a) 250°C, b) 300°C and 320°C and SbOl-AON3 monomer precursor was hot-injected into ODE while holding the temperature for 10 min. d) X-ray patterns of CoSb₂ nanoparticles prepared at 250°C, 300°C and 320°C. By varying the reaction temperature from 250°C to 320°C, the diameter of the resulting nanocrystal-

Fig. 4. XRD diffraction patterns of CoSb₂ nanoparticles prepared by thermolysis of SbOl-AON3 and CoOl-CSM. The temperature of CoOl-CSM in ODE was increased to 320°C and SbOl-AON3 was hot-injected into ODE and while holding the temperature for 10 min; in the conventional heating method, the temperature of SbOl-AON3 and CoOl-CSM in ODE were found to increase to 320°C with holding of 10 min.

Fig. 5. SEM images of CoSb₂ nanoparticles prepared by thermolysis of SbOl-AON3 and CoOl-CSM at different reaction temperatures. The temperature of CoOl-CSM in ODE was increased to (a) 250°C, (b) 300°C and 320°C and SbOl-AON3 was hot-injected into ODE while holding the temperature for 10 min. (d) X-ray patterns of CoSb₂ nanoparticles prepared at 250°C, 300°C and 320°C.

lites can be tuned at the fixed reaction time (10 min). When the reaction temperature was increased, the particle size was found to increase linearly. The crystallinity of the CoSb₂ nanoparticles prepared at 250°C is amorphous phase without any peaks. CoSb₂ structural peaks start to appear at 300°C and dominant peaks with high crystallinity are synthesized at 320°C. When free OA exists during the reaction, free carboxylic acid will react with the atoms on the surface of the nucleated particles as a reverse reaction, bind to metal atoms and start to leach out as a metal oleate. The

Fig. 6. SEM images of CoSb_2 nanoparticles prepared by thermolysis of SbOI-AON3 and CoOI-CSM at different reaction times. The temperature of CoOI-CSM in ODE was increased to a) 320°C and SbOI-AON3 was hot-injected into ODE while holding the temperature for (a) 10 min, (b) 30 min and (c) 60 min; (d) the variation of the particle size of Co-Sb nanoparticles depending on reaction time. The particle size was analyzed using the ImageJ program (○) and calculated using the Debye-Scherrer method (■).

spherical shape of the particles mainly forms because the morphology is thermodynamically more stable than other morphologies in these reaction conditions. However, when the reaction time was prolonged, different morphologies started to appear with irregular crystal growth. This is because the chemical structure of carboxylic acid will decompose under the existence of CoSb_2 nanoparticles, which will serve as catalysts at high temperature. To summarize, small amounts of carboxylic acid will enhance the nucleation of nanoparticles. An optimum amount of carboxylic acid will produce monodispersed nanoparticles. However, a prolonged reaction time will cause the decomposition of carboxylic acid, resulting in large size particles with irregular morphologies.

Figure 6 SEM shows images of CoSb_2 nanoparticles prepared by thermolysis of SbOI-AON3 and CoOI-CSM at different reaction times. The temperature of the CoOI-CSM in ODE was increased to a) 320°C and SbOI-AON3 was hot-injected into ODE while holding the temperature for a) 10 min, b) 30 min and c) 60 min; d) variation of the particle size of Co-Sb nanoparticles depending on the reaction time. The particle size was analyzed using the ImageJ program (○) and calculated using the Debye-Scherrer method (■). The particle size of CoSb_2 nanoparticles by hot-injection of SbOI-AON3 at 320°C for 10 min to 60 min was found to linearly increase from 15 nm to 65 nm, as analyzed by the Image J software. The growth rate of CoSb_2 nanoparticles was about 1 nm/min. Also, the crystal size, calculated using the Debye-Scherrer equation, was found to linearly increase from 22 nm to 32 nm with the growth rate of 0.2 nm/min. Fig. 7.

Fig. 7. XRD diffraction patterns of CoSb_2 nanoparticles prepared by thermolysis of SbOI-AON3 and CoOI-CSM at different reaction times. The temperature of CoOI-CSM in ODE was increased to 320°C and SbOI-AON3 was hot-injected into ODE while holding the temperature for (a) 10 min, (b) 30 min and (c) 60 min.

Fig. 8. XPS survey spectrum of CoSb_2 nanoparticles prepared by thermolysis of hydrated CoOI-CSM and non-hydrate SbOI-AON3 .

XRD diffraction patterns of CoSb_2 nanoparticles prepared by thermolysis of SbOI-AON3 and CoOI-CSM at different reaction times. The temperature of CoOI-CSM in ODE was found to increase to a) 320°C and SbOI-AON3 was hot-injected into ODE while holding the temperature for 10 min, 30 min and 60 min. When the reaction time was prolonged, the crystallinity of the CoSb_2 nanoparticles improved.

Figure 8 shows a typical XPS survey spectrum of Co-Sb nanoparticles prepared by thermolysis of hydrated CoOI made by exchanging the cobalt ion with NaOI and the non-hydrate SbOI prepared with antimony chloride and OA. Carbon and chloride peaks, belonging to the OA and unreacted metal chloride, respectively, were also defined. The Co2p spectrum shows a complex structure broadened by

multiple splitting effects, the peaks at 778.4 and 794.2 eV being characteristic of metallic cobalt. Also, the three peaks at 797, 780.6 and 788 eV are characteristic of CoO and the two peaks at 779.7 and 780 eV correspond to Co_3O_4 . This means that a passive oxide layer is formed on the surface of the Co-Sb nanoparticles during the thermolysis of hydrated CoOl and/or washing of the Co-Sb nanoparticles with organic solvent and EtOH. Unknown peaks between 779 and 791 eV are co-complexes such as CoOl, with different valences. Concerning the antimony spectrum, the two peaks at 152.6 and 768.5 eV are characteristic of Sb and the two peaks at 34.5 and 530 eV are allocated to Sb_2O_3 . The peak at 540.6 eV can be attributed to diantimonytetraoxide (Sb_2O_4).

4. Conclusions

A novel approach for the synthesis of CoSb_2 nanoparticles is successively demonstrated by in-situ thermolysis of hydrated CoOl and non-hydrated SbOl complexes. The synthesis of CoSb_2 nanoparticles involves the reaction of metal chloride and carboxylic acid to synthesize the non-hydrated SbOl complexes; this is followed by the thermolysis of CoOl and SbOl in non-coordination solvent. Especially, antimony trichloride is used to directly coordinate the equimolar of metal ions with OA, resulting in non-hydrated SbOl. The hot-injection method was used to overcome the different decomposition temperatures of the non-hydrated SbOl and hydrate CoOl. The particle sizes of CoSb_2 synthesized by thermolysis of metal oleate can be tuned by changing the reaction time and temperature. From the crystallographic analysis of the as-synthesized CoSb_2 nanoparticles, the particle has a single phase without any impurity phase. XPS analysis revealed that the surface of the CoSb_2 nanoparticles is passivated by a thin oxide layer.

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