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 ºC. 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 ºC is amorphous phase without any peaks. CoSb$_2$ structural peaks start to appear at 300 ºC and dominant peaks with high crystallinity are synthesized at 320 ºC. 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. Among all battery technologies, Li-ion batteries exceed any rival technology by at least a factor 2.5 in terms of energy density. 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. 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 microsized 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. 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.

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. Hyeon et al. report on the nucleation kinetics of iron oxide nanocrystals during thermolysis of the FeOl complex in a high boiling point solvent. 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. Uniform sphere-like Co-doped iron oxide nanoparticles have also been studied in the thermolysis of FeOl and CoOl.
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. In this work, nearly monodisperse, strongly crystalline, superparamagnetic CoFe$_2$O$_4$ 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. 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, PFI27) and cationic (cetyltrimethyl ammonium bromide, CTAB) surfactants.

Table 1. Sample Notation and Composition of CoOl and SbOl

<table>
<thead>
<tr>
<th>Sample notation</th>
<th>Metal source (C, A)</th>
<th>Surfactant (S, O)</th>
<th>Solvent (M, N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoOl-CSM</td>
<td>CoCl$_2$·6H$_2$O</td>
<td>Na Oleate</td>
<td>Mixture of hexane, EtOH and water</td>
</tr>
<tr>
<td>SbOl-AONx ($x = 2,3,4$)</td>
<td>SbCl$_3$</td>
<td>Oleic acid</td>
<td>None</td>
</tr>
</tbody>
</table>


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 (CoCl$_2$·6H$_2$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, CH$_3$(CH$_2$)$_7$OH) 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 method by directly reacting cobalt(II) chloride and NaOl. Briefly, 4.758 g of CoCl$_2$·6H$_2$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 method 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
were collected for analysis. The sample notation and preparation methods are described in Table 1. For example, 2 mmol (1.244 g) CoOl 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 temperatures, the solution of SbOl 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 CoSb$_2$ Nanoparticles had occurred. After the desired holding time, the mixture was cooled to room temperature. The lipid-coated CoSb$_2$ 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 CoSb$_2$ 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 Shidazu. 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 by drop-sieving the samples on the surface of a facet of diamond ATR without any specific preparation of the specimens. Differential scanning calorimetry (DSC) was performed using a DSC 50 from Shidazu. 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 2200PC 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 VersaProbeTM from Ulvac. Particle size was calculated using FWHM (Full Width at Half Max) and Scherrer’s formula,\textsuperscript{20}

\[
t = \left( \frac{K \times \lambda}{B \times \cos \theta B} \right)
\]

\((t = \text{thickness of crystallite, } K = \text{constant dependent on crystallite shape (0.89), } \lambda = \text{x-ray wavelength, } B = \text{FWHM or integral breadth, } \theta B = \text{Bragg angle}).\)

3. Results and Discussion

In our synthesis strategy, CoSb$_2$ nanoparticles are synthesized by “hot-injection” method in which non-hydrated SbOl dissolved in ODE is directly injected into a hot solution of hydrated CoOl 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 CoSb$_2$ nanoparticles. Especially, because the reaction activities of the hydrated CoOl and the non-hydrated SbOl precursors differ from each other, a separated nucleus will be generated and grow into a heterogeneous structure. A hydrated CoOl complex was advantageously prepared\textsuperscript{13} 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, carboxylic acid groups in monobasic carboxylic acid are ionized by neutralization with metal ions. Typical reaction equations for hydrated CoOl and non-hydrate SbOl complexes are described as follows:

\[
\text{CaCl}_2 + 6\text{H}_2\text{O} + 2\text{CH}_3\text{CH}_2\text{COOH} = \text{CH}_3\text{CH}_2\text{COO}\text{Na} + \text{Co(C}_2\text{H}_3\text{COO})_2 + 2\text{NaCl}
\]

(2)

\[
\text{SbCl}_3 + 3\text{CH}_3\text{CH}_2\text{COOH} = \text{CH}_3\text{CH}_2\text{COOL} + 3\text{HCl}
\]

(3)

Non-hydrated CoOl as an organometallic precursor is less suitable than hydrated CoOl for the synthesis of CoSb$_2$ by thermolysis. The particle sizes of CoSb$_2$ are tuned using equimolar ratios of metal ions and carboxylic acid, without excessive passivating surfactant/solvent. Especially, the molecular structures of non-hydrated SbOl complexes are strongly correlated to the molar ratio of Sb/OA, and the correlation of coordination modes; the thermal behavior of non-hydrated SbOl and their particle formation are investigated.

The molecular structures and thermal behaviors of non-hydrated SbOl and hydrated CoOl complexes were determined by FTIR, DSC, TGA and DTA. The solid waxy forms of non-hydrated SbOl and hydrated CoOl complexes were subjected to thermal analysis to study the reaction mechanism of nanoparticle formation. Based on FTIR data, non-hydrated SbOl samples can be seen to be a mixture of OA and SbOl with different coordination modes. The first transition appears at 131°C for hydrated CoOl-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 Co$^{2+}$. According to Bronstein, the second transition appears at 131°C for the crude hydrated CoOl-CSM sample due to the removal of chemically absorbed water,\textsuperscript{21} whereas no such endothermic peak appeared for non-hydrated SbOl. The absence of this endothermic peak is supplementary evidence supporting the prediction of the
FTIR as can be seen in Fig. 1(a), the first endothermic peak of the non-hydrated SbOl 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 SbOl-AON4 complexes, for example, the onset 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 SbOl samples as a shallow exothermic peak. According to Bronstein and Hyeon¹⁸,²¹ 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 SbOl complexes, the amount of OA is increased from SbOl-AON2 to SbOl-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 SbOl-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 CoOl-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 SbOl complexes and hydrated CoOl. Fig. 2 shows FTIR spectra of non-hydrated SbOl complexes prepared by varying the molar ratio
of SbCl₃ to OA from 1/2 to 1/4. Compared to pure OA, several new peaks appear in the region of 1,650 - 1,500 cm⁻¹ in all non-hydrated SbOl samples due to newly formed antimony carboxylate; also, a peak appearing at 1,435 cm⁻¹ is also assigned to carboxylate vibration. 1,558, 1,539 and 1,517 cm⁻¹ are assigned to the νₐ(COO) of the non-hydrated SbOl complexes, among which the band at 1,558 cm⁻¹ has the strongest intensity. A very small peak at 1,654 cm⁻¹ appeared in the SbOl-AON4, and can be assigned to C = 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 cm⁻¹ increased with the decreasing ratio of SbCl₃ and OA, with SbOl-AON4 displaying the strongest intensity of 1,702 cm⁻¹ band, which could be explained by the increasing amount of solid dimerized unreacted OA. The distinguished peaks appeared at 1,435 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 cm⁻¹, resulting in a new Δ = 81 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 cm⁻¹, several new peaks were identified as metal carboxylate bands; three bands at 1,558, 1,539 and 1,517 cm⁻¹ were assigned to asymmetrical carboxylate vibration, whereas the strong band appearing at 1,435 cm⁻¹ was assigned to symmetrical vibration. In Fig. 4, a major peak can be observed to have appeared at 1,702 cm⁻¹; this peak can be assigned to the C = O stretching band of OA or to asymmetrical vibration of unidentate mode. The intensities of the bands between 1,698 and 1,702 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. For Δ > 200 cm⁻¹, the unidentate mode can be expected; for 110 cm⁻¹ < Δ < 200 cm⁻¹, it is the bridging mode; and for Δ < 110 cm⁻¹, it is the bidentate mode. The difference between characteristic bands within the ν(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 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 nanoparticles prepared by thermal decomposition of hydrated CoOl and non-hydrated SbOl complexes.

Scheme 1. Illustration of the CoSb₂ nanoparticles prepared by thermal decomposition of hydrated CoOl and non-hydrated SbOl complexes.

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

Fig. 3. SEM images of CoSb₂ 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, and b) the temperature of SbOl-AON3 and CoOl-CSM in ODE was increased to 320°C while holding the temperature for 10 min.
Co-Sb nanocrystals 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 CoSb nanoparticles 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. 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 CoSb nanoparticles 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 while holding the temperature for 10 min. The crystallinity of the CoSb2 nanoparticles prepared by thermolysis of 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 while holding the temperature for 10 min. (d) X-ray patterns of CoSb2 nanoparticles prepared at 250°C, 300°C and 320°C.

Figure 5 shows SEM images of CoSb2 nanoparticles prepared by thermolysis of SbOl-AON3 and CoOl-CSM at different reaction temperatures. 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. When the reaction temperature was increased, the particle size increased with the growth of size until a maximum is reached. Based on these results, further experiments were performed using the hot-injection method.
The 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 SbOl-AON3 and CoOl-CSM at different reaction times. The temperature of CoOl-CSM in ODE was increased to a) 320°C and SbOl-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 (o) and calculated using the Debye-Scherrer method (●).

XRD diffraction patterns of CoSb$_2$ nanoparticles prepared by thermolysis of SbOl-AON3 and CoOl-CSM at different reaction times. 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 (a) 10 min, (b) 30 min and (c) 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 CoOl-CSM and non-hydrate SbOl-AON3. 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$_3$O$_4$. This means that a passive oxide layer is formed on the surface of the Co-Sb nanoparticles during the thermolysis of hydrated CoOI 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 CoOA, 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$_2$O$_3$. The peak at 540.6 eV can be attributed to diantimonitytroxide (Sb$_2$O$_5$).

4. Conclusions

A novel approach for the synthesis of CoSb$_2$ nanoparticles is successively demonstrated by in-situ thermolysis of hydrated CoOI 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 CoOI 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 CoOI. 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.

REFERENCES

