Nano Science and Nano Technology
An Indian Journal

Trade Science Inc.

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Synthesis of well-dispersed nano-CoSb$_3$ within mesoporous carbon

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ABSTRACT

The well-dispersed CoSb$_3$ nanoparticles within mesoporous carbon had been fabricated by wet-impregnation followed by reduction route. X-ray diffractometer (XRD) and transmission electron microscope (TEM) were used to analyze the synthetic process. These CoSb$_3$ nanoparticles had spherical morphologies with sizes around 20 nm. The use of mesoporous carbon effectively avoided the aggregation of these CoSb$_3$ nanoparticles and kept them dispersed well. The results showed the proper ratio of Sb/Co (= 5), a short reaction duration and high temperature played key roles on obtaining pure CoSb$_3$.   © 2011 Trade Science Inc. - INDIA

INTRODUCTION

As one alternative way to harvest wast industrial heat and solar energy, TE materials provide us a better way to alleviate the energy shortage. The key to realize superior thermoelectric materials is the improvement of the thermoelectric Figure of merit[1]. It requires both the decrease of thermal conductivity and simultanously the increase of the electrical conductivity[2, 3]. The alternative route is to reduce the dimensionality of typical materials into nanoscale[4-7]. By doing so, thermal conductivity could be greatly reduced through the increased grain boundary phonon scattering and lattice thermal conductivity in nano-grains could be reduced, as well[8, 9]. Yet, the electrical conductivity would be reduced accordingly[10]. Thus, an optimum microstructure might be a good combination of coase and fine grains in an

individual material. In such presumption, a composite with connective coarse grains and dispersed nano-grains is always fabricated so that electrical resistivity of the mixed grains may be kept almost unchanged while the thermal conductivity may be reduced greatly because the difference between free path of phonons and electrons[11, 12].

On the other hand, this above so-called nano-effects in a bulk thermoelectric material, could be remarkable only if some construction units (grains, particles, etc.) in the material were smaller than a few tens of nanometers or even a few nanometers[13]. Unfortunately, such small particles were generally thermodynamically unstable and easily grew up and coarsened into micrometers particles through self-aggregation due to their high density of boundaries when they were further prepared into bulk body through module preparation and

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calcination at elevated temperatures. Therefore, solutions should be attempted to hindering the coarsening in nanostructures, such as adding secondary nanoparticles by blending route[14, 15] or *in situ* route[16].

In this study, a novel nano-TE composite was fabricated (Scheme 1): $CoSb_3$ nanoparticles well-dispersed in mesoporous carbon. Firstly, due to the confinement of mesoporous channels (in most cases, less than several tens of nanometers), the aggregation of nanoparticles could be effectively restrained during the synthesis of nano-$CoSb_3$ particles at high temperature. Secondly, because these mesoporous composite powders were usually in the size of micrometers, it could be convenient for them to be blended with other micrometer-size $CoSb_3$ powders and then, further to be prepared into bulk body without worrying about the self-aggregation of these nano-TE powders. Finally, mesoporous materials themselves had low thermal conductivity due to their high porosities and large amount of defects on surface, which were helpful to improve the ZT value of thermoelectric materials.

A, infiltration with inorganic precursor;
B, pre-reduction by NaBH₄;
C, CoSb₃ synthesis in high temperature;
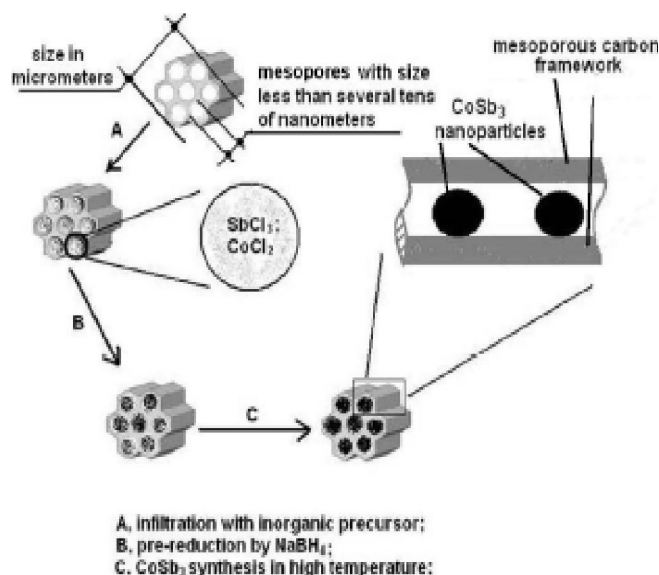
Scheme 1 : Illustration for the formation of CoSb₃ dispersed within the mesopores of mesoporous carbon.

EXPERIMENTAL PROCEDURE

The mesoporous carbon was synthesized by using mesoporous SBA-15 silica as template according to literature[17]. Typically, 1 g of SBA-15 was added to a sucrose solution by dissolving 1.25 g of sucrose and 0.14 g of H_2SO_4 in 5 g of H_2O. The mixture was placed in a drying oven for 6 h at 373 K, and then for 6h at 433 K. Then, it was treated again at 373 K and 433 K for another 12 h after the addition of 0.8 g of sucrose, 0.09 g of H_2SO_4 and 5 g of H_2O. The carbonization was completed by pyrolysis with heating to typically 1173 K for 5 h under vacuum. The pure mesoporous carbon was obtained after washing the pyrolysized mixture with 5 wt % hydrofluoric acid at room temperature, to remove the silica template.

Co and Sb precursors/mesoporous carbon composites with various ratio of Sb/Co (4-6) were achieved by wet-impregnation. Typically, sample S5-500-45 (with the molar ratio of Sb/Co = 5) was prepared as follows: 0.13 g cobalt(II) chloride hexahydrate and 0.76 g antimony trichloride were added to citric acidic ($C_6H_8O_7$) ethanol solution by dissolving 0.47 g citric acid in 7 mL absolute ethanol. Then, mesoporous carbon (1.0 g) was dispersed into the above solution with stirring. After stirred for 2.5 h, the mixture was transferred into an open Petri dish to evaporate ethanol. After the mixture was dried, the Co-Sb precursors confined within mesoporous carbon powders were achieved.

$NaBH_4$ solution were prepared by dissolving 0.2 g $NaBH_4$ and 0.2 g NaOH into a mixed solvent with 1.0 ml ethanol and 1.0 ml distilled water.
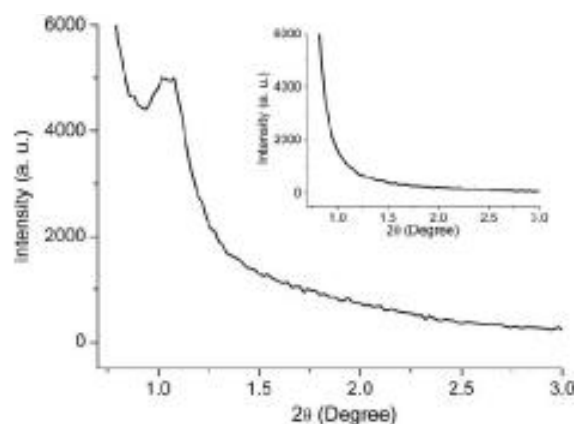
The $NaBH_4$ solution above was added into the Co and Sb precursors/mesoporous carbon composite powder drop by drop with slow stirring. Because of the heat released from the reductive reaction, solvent would evaporate gradually and the mixture was further kept drying. After the reductant solution was consumed, the reduced powder further suffered from heat-treatment in a tube furnace under designed temperature (500 ºC) and held for a period of time (45 min) under 5 % H_2/ 95 % N_2 mixed atmosphere. The synthesized powder was washed three times with ethanol and distilled water, respectively, followed by drying. The samples were named as Sr-T-t, here, 'r' referring to the ratio of Sb/Co; 'T', the temperature by heat-treatment; 't', the duration at the designed temperature T.

Powder XRD patterns were recorded by using a Rigaku D/Max 2200PC diffractometer with $Cu_{K\alpha}$ radiation (40 kV and 40 mA) with a scanning rate of 0.6 min⁻¹ for small-angle testing and 10º min⁻¹ for large-
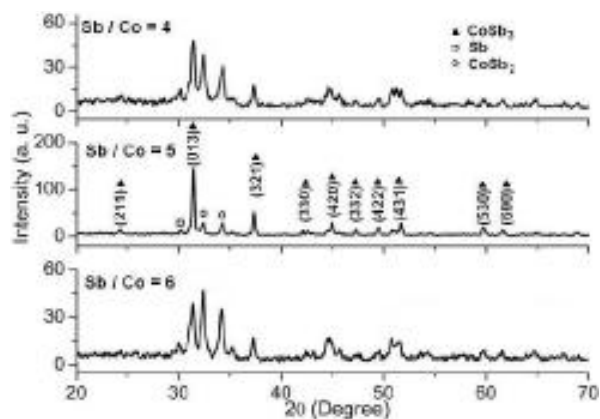
angle testing. TEM image was obtained on a JEOL-2010F electron microscope operated at 200 kV.

RESULTS AND DISCUSSION

Figure 1a shows the small angle XRD pattern (SAXRD) of mesoporous carbon before and after nano- $CoSb_3$ loaded. One major peak at about 1° can be observed which indicates the ordering of mesopore structure before nano-$CoSb_3$ loaded. After nano-$CoSb_3$ loaded, the ordering of mesopore structure disappeared according to the SAXRD (Figure 1a, inset). This phemonon indicates most of mesopores were filled with nano-$CoSb_3$ particles which was consistent with the observation of TEM (Figure 2). Apart from the mesopores partially filled, part of mesoporous framework collapsed during the heat-treatment under H_2 atmosphere.

The WAXRD patterns of the products (Figure 1b) prepared with various ratios of precursors at 500 °C for 45 min demonstrate that ralative high Sb/Co ratio was necessary in view of the high volatile of antimonide, although the molar ratio of Sb/Co should be 3 according to the chemical formula of $CoSb_3$. In this experiment, the proper ratio was 5, at which pure $CoSb_3$ with skutterudite structure (PDF 65-3144) was obtained. A second main phase, $CoSb_2$ (PDF 65-4102), was found when the ratio was higher or lower than 5, especially for S6-500-45 (TABLE 1).

TABLE 1 : Phase compositions of the products obtained at the various synthesis conditions.

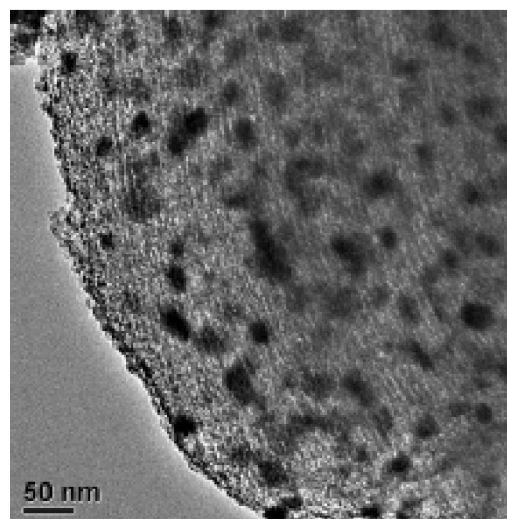| Sample	Molar ratios of Co : Sb	Main phase	Phase composition
S4-500-45	1 : 4	$CoSb_3$	$CoSb_3 + CoSb_2$
S5-500-45	1 : 5	$CoSb_3$	$CoSb_3$
S6-500-45	1 : 6	$CoSb_2$	$CoSb_2 + CoSb_3$

Figure 2 : TEM images for nano-CoSb₃/mesoporous carbon composite (S5-500-45).

TEM investigation provides the direct observation of the morphology and distribution of $CoSb_3$ nanoparticles in mesoporous carbon (sample S5-500-45). Uniform $CoSb_3$ spherical nanoparticles with diameters around 20 nm can be clearly seen in the sample S5-500-45. These nanoparticles are well dispersed among the pore chanells of mesoporous carbon. Obviously, due to the confinement of pore channels, these nanoparticles were well dispersed even after calcination at elevated temperature. Therefore, it could be deduced that mesoporous carbon has been success-

(a)

(b)

Figure 1 : Small angle XRD patterns for the mesoporous carbon before (a) and after (inset, in (a), for sample 5-500-45) CoSb₃ nanoparticles loading. Wide angle XRD patterns for samples prepared at various ratio of Sb/Co at 500 °C for 45 min (b).

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fully used as supporter to prepare well-dispersed $CoSb_3$ nanoparticles. In contrast to literatures[8] in which pure H_2 was used as redutive and protective atmosphere, this experiment used much more safter atmosphere with 5 % H_2 with N_2, which gave a practical way to prepare TE materials.

The usage of citric acid and $NaBH_4$ are important to synthesis nano-$CoSb_3$/mesoporous carbon composite. Several researchers decreased the evaporation of Sb^{3+} (in the form of Sb_2O_5) by pre-reducing Sb^{3+} into metal Sb[18]. In this experiment, however, it was insufficient. Using only $NaBH_4$ as reduction agent but without citric acid as complexing agent, $CoSb_2$ was found to be the main phase to co-exist with $CoSb_3$ as a second phase in all temperatures. In contrast, citric acid could effectively suppress the evaporation of intermediate products-metal Sb nanoparticles.

The experimental results showed that both the synthesis temperature and duration played key roles on determining the phase composition of the final products. The formation of the $CoSb_3$ phase took place in a stepwise mode: firstly, metal Co and Sb were reduced by $NaBH_4$ at the first step; secondly, the intermediate phase - $CoSb_2$, emerged when the reduced metal nanoparticles were further treated under high temperature; and finally, the final product, $CoSb_3$ was formed. The possible reaction process is presented in the following chemical reactions:

$$CoCl_2 + 2NaBH_4 \rightarrow Co + 2BH_3 + 2NaCl + H_2 \qquad (1)$$
$$SbCl_3 + 6NaBH_4 \rightarrow 2Sb + 6BH_3 + 6NaCl + 3H_2 \qquad (2)$$
$$Co + 2Sb \rightarrow CoSb_2 \qquad (3)$$
$$CoSb_2 + Sb \rightarrow CoSb_3 \qquad (4)$$

Apart from the formation of $CoSb_3$, there is a side reaction: $CoSb_3$ is unstable and would decompose at high temperature to form $CoSb_2$ and antimony.

$$CoSb_3 \rightarrow CoSb_2 + Sb\uparrow \qquad (5)$$

As shown in Figure 3a, when the reaction was prolonged to 15 min at 450 °C, the product consists of $CoSb_3$ as main phase, small amount of unreacted $CoSb_2$ and Sb as second phase. This result indicates 15 min of reaction duration at 450 °C is long enough to form $CoSb_3$. When duration increased to 45 min, however, much more $CoSb_2$, Sb were found, which indicated that the $CoSb_3$, as an unstable phase, decomposed (reaction (5)). Similar phenomenon was also found in the synthesis of $CoSb_3$ *via* mechanical alloying process[19]
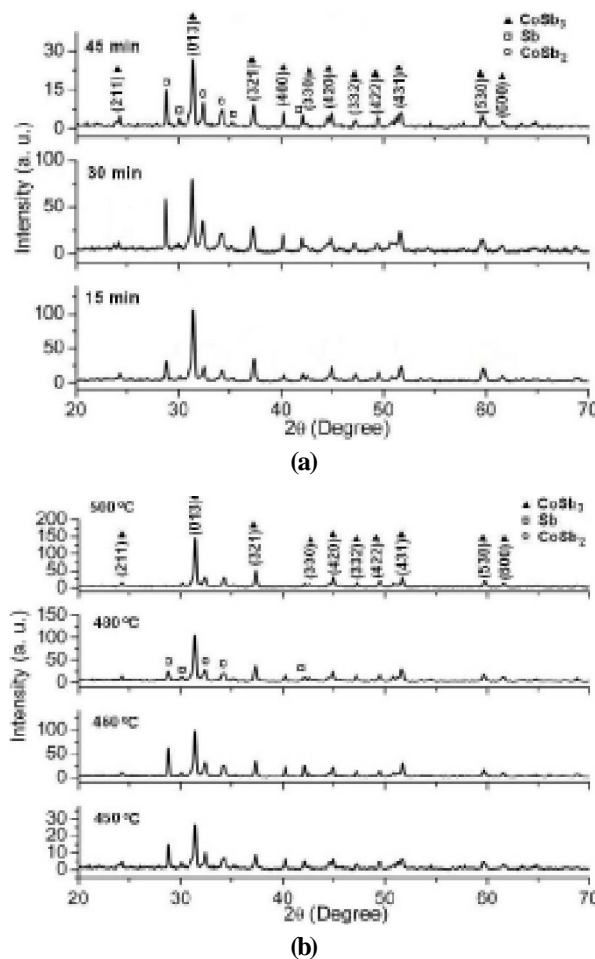
(a)

(b)

Figure 3 : Powder XRD patterns for the products prepared at various synthetic conditions. Left, various durations at ratio of 5 for Sb/Co and 450 °C; righ, various temperature at ratio of 5 for Sb/Co and for a duration of 45 min.

and polyol process[11] in which prolonged milling time or reaction duration led to the decomposition of $CoSb_3$ into $CoSb_2$ and Sb. In contrast to reaction duration, the reaction temperature played a positive role on the formation of $CoSb_3$ (Figure 3b). The difference between the reaction speeds of reaction (4) and reaction (5) greatly increases as the reaction temperature increases: the speed of reaction (4) at 500 °C is much higher than that of 450 °C while the speed of reaction (5) is almost constant from 450 °C to 500 °C. Therefore, at a temperature as 500 °C, the speed of reaction (4) was much higher than that of reaction (5), greatly. As a result, pure $CoSb_3$ was obtained at 500 °C.

CONCLUSIONS

Pure and well dispersed $CoSb_3$ nanoparticles have

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been succussfully synthesized by using mesoporous carbon as supporter. Both proper ratio of Sb/Co (Sb/Co = 5) and certain amount of complexing agent (citric acid) were necessary for the sucessful synthesis. The synthesis of the $CoSb_3$ phase followed stepwise mode with $CoSb_2$ as an intermediate product. A short reaction duration and high temperature were preferred for the preparation of pure $CoSb_3$ phase. The properties of the novel materials are under way.

ACKNOWLEDGMENTS

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