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Organic–Inorganic Nanohybrids as Novel Thermoelectric Materials: Hybrids of Polyaniline and Bismuth(III) Telluride Nanoparticles

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Thermoelectric materials have received much attention recently from the viewpoint of global environmental issues and effective utilization of energy resources. Especially those effective at relatively low temperature, such as below 100°C, which are usually abandoned without use, have become noteworthy recently. From this point of view, organic thermoelectric materials are most attractive, because they could be prepared at low cost and applied in various locations due to their flexibility. We have investigated the thermoelectric properties of organic conducting polymers such as polyaniline, polypyrrole, and polyphenylenevinylene, and succeeded in increasing the thermoelectric performance by selecting dopants, stretching conducting films, etc. Recently we have focused on new systems of organic–inorganic hybrid thermoelectric materials. Herein we present the preparation of a novel system of hybrids of polyaniline and bismuth(III) telluride nanoparticles, starting from bismuth(III) chloride and tetrachlorotellurium by using polyvinylpyrrolidone as a protecting reagent, as well as their thermoelectric properties. The hybrids prepared by this particular method showed much higher thermoelectric performance than the starting organic conducting polymer.

Key words: Hybrid thermoelectric materials, bismuth(III) telluride, nanoparticles, polyaniline, Bi_2Te_3, reduction, bismuth(III) chloride, tetrachlorotellurium, tetraethylene glycol, Seebeck coefficient, thermoelectric power factor

INTRODUCTION

Recently, thermoelectric materials, especially those effective at relatively low temperature such as below 100°C, have received much attention because the recovery of even low-grade thermal energy is required to utilize fossil fuels effectively. However, there are few known thermoelectric materials which are effective at relatively low temperature. Bismuth(III) telluride Bi_2Te_3 could be the only example.

On the other hand we have investigated organic thermoelectric materials, especially those composed of organic electroconducting polymers such as polyaniline,[1–4] polypyrrole,[5] and polyphenylenevinylene derivatives.[6,7] Although the conducting polymers decompose at high temperature, they are relatively stable against heat among organic materials. A few conducting polymers such as polyacetylene prepared by special methods have a high electric conductivity, but are not stable in air. In contrast, aromatic organic conducting polymers such as polyaniline, polypyrrole, and polythiophene do not show such high conductivity, but are stable under air and against heat, for example, at 250°C or 300°C. Thus, aromatic electroconducting polymers are used for practical purposes such as electric batteries, electroconducting films, charge-dissipation coatings, electromagnetic interference shielding,

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actuators, sensors, catalysts, electroluminescent materials, etc. Although these aromatic conducting polymers have advantages such as low cost, plenty of resources, easy processability, and flexible-film formation, their thermoelectric performance are not high enough for use as practical thermoelectric materials.[7] Thus, we have tried to improve the performance by hybridization between organic conducting polymers and inorganic bismuth(III) telluride. For this purpose, nanoparticles of inorganic bismuth(III) telluride have been prepared by a chemical method. Previously we successfully prepared Bi_2Te_3 nanoparticles by treatment of $BiCl_3$ and $Te(OC_2H_5)_4$ with $NaBH_4$.[8] However, this method requires special techniques. Here, we prepared Bi_2Te_3 nanoparticles by an easier route, starting from less expensive starting materials, $BiCl_3$ and $TeCl_4$, and then prepared hybrid materials by using these Bi_2Te_3 nanoparticles and conducting polyaniline.

EXPERIMENTAL PROCEDURES

Preparation of Bi_2Te_3 Nanoparticles

Bismuth(III) chloride ($BiCl_3$, 1.8 mmol), tetrachlorotellurium ($TeCl_4$, 2.7 mmol), and poly(*N*-vinyl-2-pyrrolidone) (PVP, 2.7 mmol in monomer unit) were added to purified (degassed and dehydrated) tetraethylene glycol (TEG, 250 mL) in a four-necked 500-mL flask. After stirring at 324 rpm for 30 min, the mixtures were treated by heat to be refluxed under nitrogen flow for 1 h with an electric mantle heater by applying a voltage of 70 V. After heat treatment, the temperature was gradually decreased. The solvent TEG was replaced with ethanol by using a centrifuge at 3000 rpm for 40 min. After washing with ethanol four times, the precipitated nanoparticles were obtained as powder by removal of the solvent under reduced pressure in air and successive drying under reduced pressure for 12 h. The obtained samples were black powders and very easily oxidized by air. The sample solution was rapidly oxidized in 10 s when exposed to air to produce gray suspensions.

Preparation of Polyaniline (PANi)

Aqueous solution of hydrochloric acid (HCl, 1 mol L^{-1}, 117 mmol) was slowly added to a 1-L round-bottomed flask containing lithium chloride (LiCl, 0.778 mmol). Aniline ($C_6H_5NH_2$, 0.054 mol) was added to the mixture. The flask containing the mixture was kept in a refrigerator to decrease the temperature, and then cooled to −30°C in cold acetone for 1 h. To this mixture, a mixed solution of ammonium peroxodisulfate [$(NH_4)_2S_2O_8$, 0.11 mol], deionized water (100 mL), and lithium chloride (LiCl, 0.67 mol) was slowly added dropwise during 50 h. After the addition, the mixture was further cooled for an additional 1 h under stirring and then the temperature was gradually increased to room temperature. The product was separated by vacuum filtration with a 0.2-μm-pore filter, washed with deionized water until the filtrate became neutral and with acetone until the filtrate acetone had no color, and then dried at 40°C under vacuum for 12 h to produce black powder. An aqueous solution of ammonia (NH_3, 1 mol L^{-1}, 100 mL) was added to the produced black powder, and the mixture was stirred for 1 h to remove the dopants from polyaniline. The polyaniline was washed with deionized water until the filtrate reached neutral pH, and then washed with acetone until the filtrate had no color. The produced polyaniline was dried under vacuum at 50°C for 12 h to obtain polyaniline with emeraldine base structure as powder.

Hybridization of Polyaniline with Bi_2Te_3 Nanoparticles

Physical Mixture

Polyaniline emeraldine base, camphorsulfonic acid, and *m*-cresol were mixed at the designed ratio. The mixtures were treated ultrasonically for 1 h and then stirred for 24 h with a magnetic stirrer. The solution was cast on a glass plate and kept in a draft chamber until dry.

Solution Mixture

Polyaniline emeraldine base (300 mg) was dissolved in 1,4-dioxane (degassed and dehydrated, 600 mL) by stirring for 48 h. Bi_2Te_3 nanoparticles were added to polyaniline solution in a glove box and stirred for 48 h. Then camphorsulfonic acid and *m*-cresol were added to the solution, and the mixtures were stirred in a glove box for 72 h under vacuum to remove 1,4-dioxane. The produced solution, cast on a glass plate, was dried until film formation.

RESULTS AND DISCUSSION

Bi_2Te_3 Nanoparticles and Polyaniline in Emeraldine Form

Here we chose bismuth(III) chloride ($BiCl_3$) and tetrachlorotellurium ($TeCl_4$) as the starting materials to produce bismuth(III) telluride (Bi_2Te_3) nanoparticles because they are easily available at low cost.

The reduction and decomposition of $BiCl_3$ and $TeCl_4$ to produce Bi_2Te_3 were carried out at high temperature in tetraethylene glycol (TEG). Poly(*N*-vinyl-2-pyrrolidone) (PVP) was used as the protecting reagent to produce Bi_2Te_3 nanoparticles. The voltage applied to the electric mantle heater was varied from 50 V to 70 V, and the best result was obtained by applying 70 V. The obtained nanoparticles were less than 10 nm in diameter based on transmission electron micrograph (TEM) observation, and exhibited the x-ray diffraction (XRD) pattern shown in Fig. 1. Figure 1 reveals that the

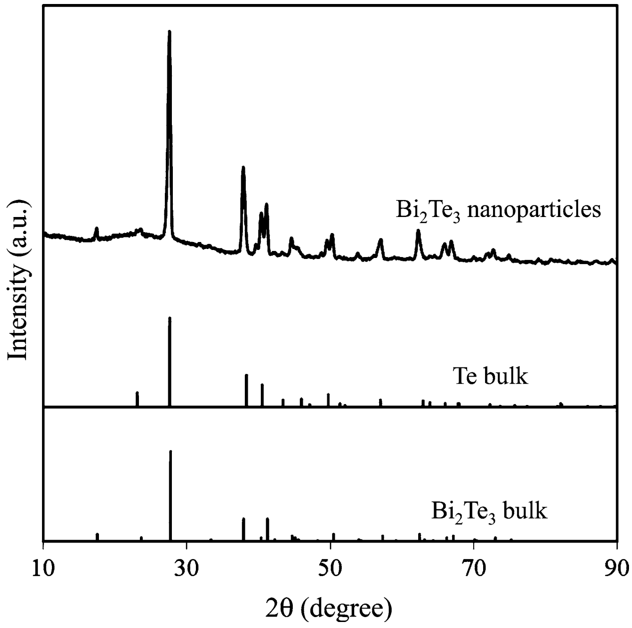

Fig. 1. XRD patterns of Bi_2Te_3 nanoparticles as well as Te and Bi_2Te_3 bulk as references.

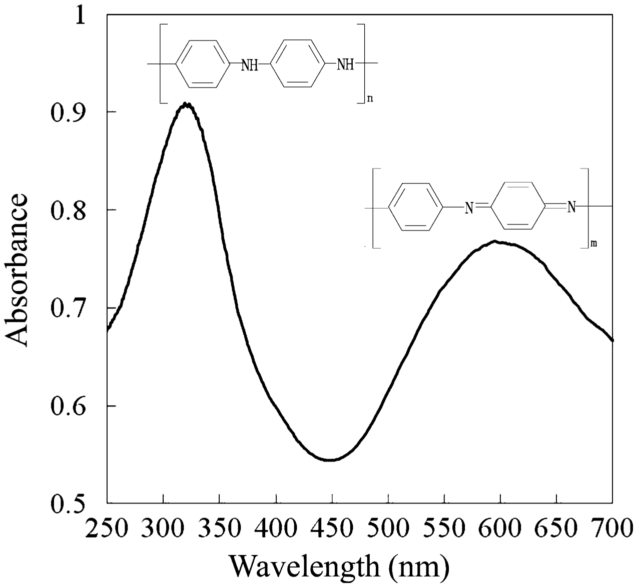

Fig. 2. UV–Vis spectrum of high-molecular-weight polyaniline in *N*-methylpyrrolidone.

obtained XRD pattern is consistent with that of Bi_2Te_3 bulk but not of Te bulk. Fourier-transform infrared (FT-IR) spectra of the Bi_2Te_3 nanoparticles suggested that most of the PVP protecting reagent decomposed during the preparation of nanoparticles.

Polyaniline in emeraldine form was obtained by polymerization of aniline at a temperature as low as −30°C, and treated with ammonia for dedoping. The emeraldine structure was confirmed by the UV–Vis spectrum of the 1-methyl-2-pyrrolidone (NMP) solution (Fig. 2). The ratio of absorbance at 323 nm against that at 639 nm, attributed to benzenoid and quinonoid structure, respectively, was observed to be 1.2, indicating emeraldine structure.

Gel permeation chromatography indicated that the weight-average molecular weight (M_w) of the produced polyaniline was calculated as 92,000 and the dispersion (M_w/M_n) was 1.1, using standard polyvinylpyridine as a reference. These data show that the obtained polyaniline has enough high molecular weight and is almost monodisperse.

Hybrid Films of Electroconducting Polyaniline and Bi_2Te_3 Nanoparticles

We succeeded in hybridization of polyaniline with Pt and Au nanoparticles and improved the thermoelectric performance twofold.[9] Here hybridization of polyaniline and Bi_2Te_3 nanoparticles was carried out by two methods: physical mixture and solution mixture. In the physical mixture, Bi_2Te_3 nanoparticles were mixed with polyaniline, camphorsulfonic acid (dopant), and *m*-cresol (second dopant) to produce nanoparticle suspensions. This is a method modified from the preparation of conducting polyaniline films by doping camphorsulfonic acid and *m*-cresol.[10] The molar ratio of polyaniline to Bi_2Te_3 (R) was 5.

In the physical mixture, *m*-cresol acts as the second dopant as well as the solvent. Thus, the Bi_2Te_3 nanoparticles were considered to be not well dispersed in the mixture. Thus, we used a solution mixture method too, in which polyaniline was first dissolved in 1,4-dioxane and the dioxane solution was mixed with Bi_2Te_3 nanoparticles (R = 1), camphorsulfonic acid, and *m*-cresol. After 1,4-dioxane was removed *in vacuo*, the mixtures were cast to produce the polyaniline hybrid films.

The XRD pattern of both hybrid films were similar to each other, composed of a relatively sharp pattern and very broad ones, attributed to Bi_2Te_3 and polyaniline, respectively, since polyaniline has a rather amorphous structure and often shows a broad, wide peak. FT-IR spectra of both films were also similar to each other, where the molar ratios of polyaniline to Bi_2Te_3 nanoparticles R were 5 and 1, for those produced by physical mixture and solution mixture, respectively. However, some films produced by solution mixture showed cracks in scanning electron microscopy (SEM). Bi_2Te_3 nanoparticles were expected to be well dispersed in the hybrid films because no precipitates were observed in the mixed solution to be cast for preparation of the film. In fact, we have direct evidence for excellent distribution of nanoparticles in the film based on TEM observation of thin cast films.

Thermoelectric Properties

The electric conductivity and Seebeck coefficient were measured for hybrid films prepared by physical mixture and solution mixture, as well as a

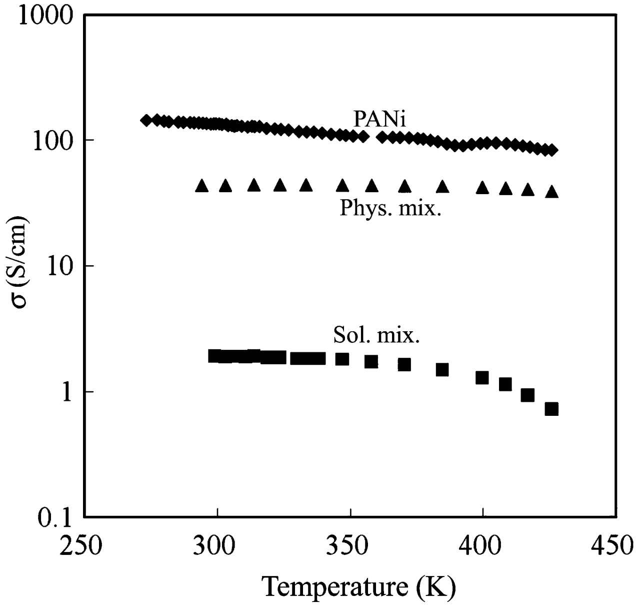

Fig. 3. Electrical conductivity (σ) of hybrid films of polyaniline and Bi_2Te_3 nanoparticles, prepared by physical mixture and solution mixture, as well as a doped polyaniline film as a reference, over a range of ca. 300 K to 425 K.

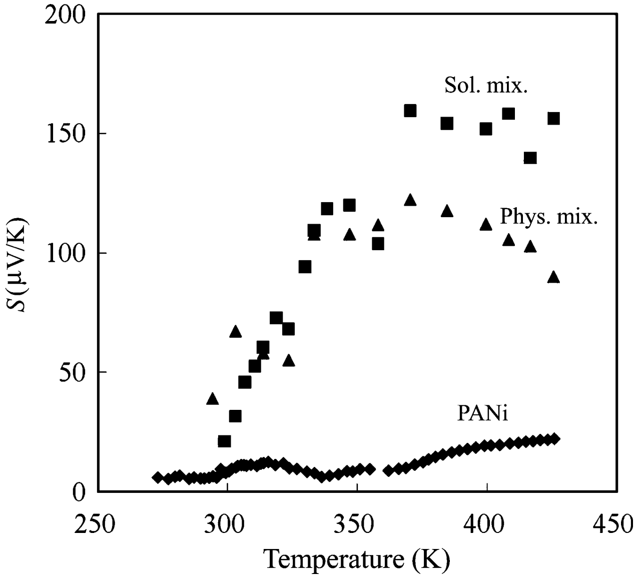

Fig. 4. Seebeck coefficient (S) of hybrid films of polyaniline and Bi_2Te_3 nanoparticles, prepared by physical mixture and solution mixture, as well as a doped polyaniline film as a reference, over a range of ca. 300 K to 425 K.

conducting polyaniline film as a reference. As described in the “Experimental Procedures” section, all films were doped with camphorsulfonic acid and *m*-cresol. The hybrid film produced by physical mixture was prepared by only mixing Bi_2Te_3 nanoparticles, polyaniline, camphorsulfonic acid, and *m*-cresol, while that produced by solution mixture was prepared in two steps, i.e., first dissolving polyaniline in 1,4-dioxane and then mixing the solution with Bi_2Te_3 nanoparticles, camphorsulfonic acid, and *m*-cresol.

The results for electric conductivity and Seebeck coefficient are shown in Figs. 3 and 4, respectively. Hybrid films showed lower electric conductivity than the doped conducting polyaniline film, although the electric conductivity of hybrid films slightly increased with increasing hybridization ratio (R, molar ratio of polyaniline in monomer unit against Bi_2Te_3 nanoparticles). Although we expected that the solution mixture method would provide hybrid films with higher conductivity because of better coordination of polyaniline to nanoparticles, the opposite was observed. This is probably because the solvent dioxane may remain on the surface of nanoparticles, resulting in aggregation of nanoparticles in the hybrid film prepared by solution mixture, which may prevent smooth contact even among polyaniline molecules. In the case of hybrid films prepared by physical mixture, the electric conductivity was rather close to that of polyanilines in comparison with those prepared by solution mixture.

For the Seebeck coefficient (Fig. 4), the hybrid films showed much higher values than the conducting polyaniline film. About one order of magnitude higher Seebeck coefficients were observed for the hybrid films in comparison with the polyaniline films. Usually it is thought that there is a trade-off between electrical conductivity and Seebeck coefficient of thermoelectric materials; i.e., when the conductivity decreases, the Seebeck coefficient will increase. This relation is observed in the present case. However, the hybrid films have got more than the lost; i.e., although the hybrid film has smaller conductivity and larger Seebeck coefficient than polyaniline film, the increase in Seebeck coefficient is more effective than the decrease in conductivity for improvement of thermoelectric property by hybridization.

The thermoelectric power factor (P) was calculated from the electrical conductivity (σ) and Seebeck coefficient (S) of the hybrid films by using Eq. 1.

$$P = S^2\sigma. \tag{1}$$

The results are shown in Fig. 5. Interestingly, the hybrid film prepared by physical mixture had much higher power factor than the conducting polyaniline film and even than the hybrid film prepared by solution mixture; for example, at 350 K, the power factor of the polyaniline film is ca. 1 μW/mK^2, while those of the hybrid films prepared by solution mixture and physical mixture are ca. 2.6 μW/mK^2 and 51 μW/mK^2, respectively. The physical mixture hybrid film has about 50 times higher power factor than the polyaniline film.

CONCLUSIONS

Bi_2Te_3 nanoparticles were prepared by reduction and decomposition of $BiCl_3$ and $TeCl_4$ in tetraethylene glycol (TEG) at high temperature in

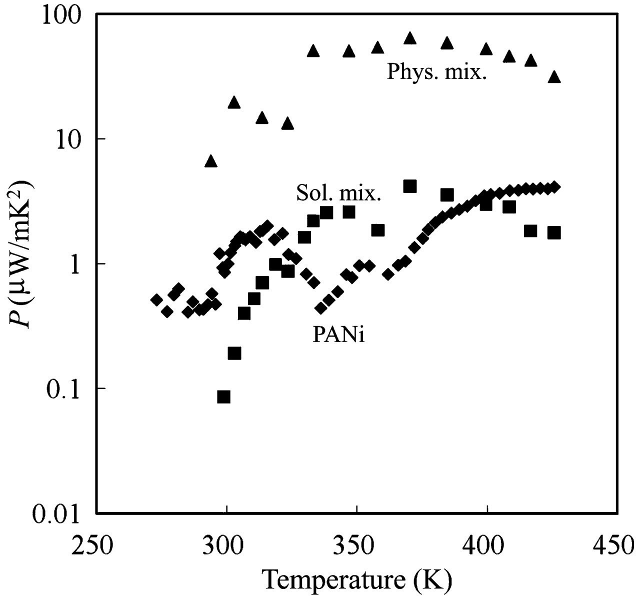

Fig. 5. Thermoelectric power factor ($P = S^2\sigma$) of hybrid films prepared by physical mixture and solution mixture, as well as a doped polyaniline film as a reference.

the presence of poly(N-vinyl-2-pyrrolidone) (PVP). Monodisperse emeraldine-form polyaniline ($M_w/M_n = 1.1$) with high molecular weight ($M_w = 92{,}000$) was prepared by oxidative polymerization of aniline with ammonium peroxodisulfate $(NH_4)_2S_2O_8$ at −30°C. The obtained Bi_2Te_3 nanoparticles and polyaniline (PANi) in emeraldine form were physically mixed with camphorsulfonic acid in m-cresol. The hybrid film obtained by casting the above mixtures (physical mixture method) had the same order of electrical conductivity as the PANi film and about one order of magnitude higher Seebeck coefficient than the PANi film. Thus, the power factor of the above hybrid film is about 50 times higher than the PANi film. We do not know why such high power factor and Seebeck coefficient were observed for the hybrid films prepared by physical mixture in comparison with those by solution mixture. However, this is certainly the effect of Bi_2Te_3 nanoparticles dispersed in polyaniline media. Based on TEM observation of the thin cast films, the nanoparticles were well dispersed in the case of physical mixture film, while aggregation of nanoparticles was observed for solution mixture films. This difference may explain the thermoelectric properties between the two types of hybrid films.

Although we have not measured the thermal conductivity κ of the films yet, the thermal conductivity (κ) of organic thermoelectric materials is usually on the order of 0.1 W/mK.[11] If this value is applied to the present system, the dimensionless thermoelectric figure of merit (ZT) derived from Eq. 2 can be calculated at a certain absolute temperature (T).

$$ZT = \frac{P}{\kappa} \cdot T. \tag{2}$$

The calculated ZT value of the hybrid films prepared by physical mixture is ca. 0.18 K at 350 K, while those of the hybrid film prepared by solution mixture and PANi films are ca. 0.009 and 0.003, respectively. If this is the case, the ZT value of ca. 0.18 will be a record value, because the highest report among organic thermoelectric materials to date is ca. 0.1.[7] However, we cannot promise that the thermal conductivity will remain at 0.1 W/mK. Development of better hybrid materials is underway with financial support from the Regional Innovation Cluster Program (global type) “Yamaguchi Green Materials Cluster” from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

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