Development of "Thermoelectric Power Generating Paper" Using Carbon-nanotube-composite Paper

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ABSTRACT

We propose a unique thermoelectric material based on a carbon-nanotube(CNT)-composite paper that a composite material of the CNT and a paper, i.e., a "thermoelectric power generating paper." Recently, it has been found that the CNTs show a giant Seebeck effect, i.e., the CNT can be the thermoelectric material. For the purpose of this study, we conducted an experiment that the thermoelectric power generation using the CNT-composite paper. As a result, the Seebeck effect was observed from the CNT-composite paper. Therefore, our CNT-composite paper can be used as the thermoelectric power generating material.

Keywords: carbon nanotube, Seebeck effect, thermoelectric material, carbon-nanotube-composite paper

1 INTRODUCTION

In recent years, about two thirds of the consumed energy is wasted as heat. As a candidate of solutions for this problem, heat recovery and power regeneration technologies have been focused. For instance, various thermoelectric materials that enable heat recovery and power regeneration efficiently have been developed by the technologies. However, since rare metals are used as existing thermoelectric materials typically, there is a limit to the resource supply. Therefore, we need a new thermoelectric material to replace those materials. Recently, it has been found that carbon nanotubes(CNTs) show a giant Seebeck effect [1]. However, it is difficult to use the CNT as the thermoelectric material generally because its size is nanoscale and it is like powder. As a solution of this problem, we have proposed a CNT-composite paper [2]. The CNT-composite paper is a composite material of the CNTs and the paper. We can utilize CNT functions easily by using the composite papers. Here, we propose the use of our CNT-composite paper for new thermoelectric material using the CNTs, i.e., a "thermoelectric power generating paper." The composite paper can be fabricated easily by the papermaking method based on the traditional Japanese *Washi* paper making process [2]. Our CNT-composite paper shows almost all functions of the CNT despite of the paper, and we can control the shape of this composite paper. Figure 1 shows a sample of CNT-composite paper.

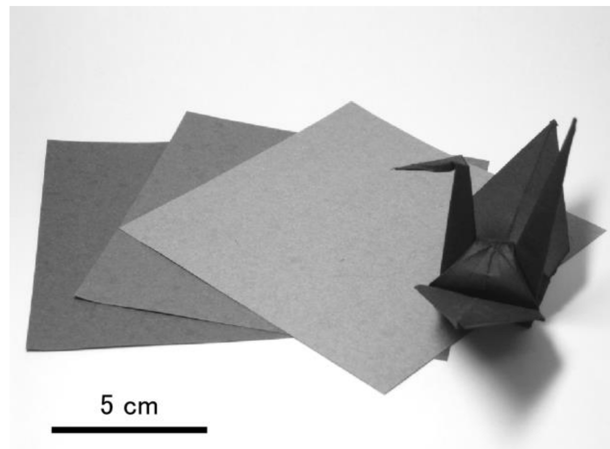

Figure 1: Samples of CNT-composite papers. Differences of color are caused by the amount of contained CNTs

To generate power by using the thermoelectric material, there are some important points. As the first point, the material has temperature difference in it. In addition, the difference should be kept. Therefore, thermal conductivity of the material should be low. In contrast, electrical conductivity of the power generating materials should be high, i.e., the thermoelectric materials should manage both low thermal and high electrical conductivities. Our CNT-composite paper is expected to realize the above request. Originally, the CNTs have the high thermal- and high electrical-conductivities. However, our composite paper has also pulp fibers that have a thermal insulation property. As the next point, a metal or a semiconductor material should be chosen to obtain the Seebeck effect. Our composite paper can show the metallic and the semiconducting properties because the contained CNT has them. Therefore, our paper is expected to be suitable materials for the thermoelectric power generation. Here, we show an actual making method for the composite paper and demonstrate that it generates power as the thermoelectric material.

2 EXPERIMENTAL METHOD

In this study, we fabricate and test our "thermoelectric power generating paper" based on the CNT-composite paper. Firstly, we here show a papermaking method for our composite paper. Then we also show a construction of our thermoelectric paper. After making the paper, we test the thermoelectric power generating ability of the sample.

2.1 Papermaking Method for CNT-Composite Paper

We fabricate the CNT-composite paper for the purpose of this study. The composite paper can be fabricated easily by the papermaking method based on the traditional Japanese *Washi* paper making process [2]. In concrete, the CNT dispersion and the pulp (paper material) dispersion are prepared firstly. Then, they are mixed and poured into a bottomless silicone case on a fine net. After that, the pulp fibers with the CNTs are remained on the encircled net by the bottomless case. Finally, the remained materials are dried to finalize the papermaking process (see Fig. 2).

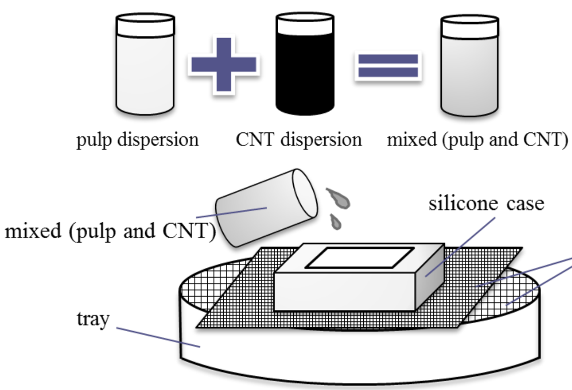

Figure 2: Schematic of papermaking method for CNT-composite paper.

2.2 Tests of Thermoelectric Power Generation

Generally, the Seebeck effect is known to have particularly giant effect in a semiconductor material [3]. Thus, we confirm the thermoelectric power generation using one sheet (piece) of the metallic (the CNT-concentration: 8.53 wt. % for weight of the pulp material) and semiconducting (0.2 wt. %) CNT-composite papers firstly. To obtain above samples, we follow the following procedures.

I-1. Preparing 14 mg of HiPco-type CNTs (single-walled CNT, provided by NanoIntegris Inc.) and 14 mg of sodium dodecyl sulfate (SDS) as a dispersant for the metallic CNT-composite paper.

I-2. Putting HiPco and SDS into 10 ml of pure water and applying ultrasonication to them for 30 minutes to prepare the metallic CNT dispersion.

II. Preparing 20 ml of a marketed semiconducting CNT dispersion (90% purity, CNT/water: 1 mg/100 ml density, NanoIntegris Inc.) for the semiconducting paper.

III. Preparing 150 mg of the pulp materials, putting them into 15 ml of pure water, and dispersing to prepare the pulp dispersion for the metallic CNT composite paper.

IV. Preparing 100 mg of the pulp materials, putting them into 10 ml of pure water, and dispersing to prepare the pulp dispersion for the semiconducting CNT composite paper.

V. Following the papermaking method as described above with the mixed dispersion made from I and III, or II and IV.

After that, we choose the semiconducting papers to use and prepare some sheets with changing the CNT-concentration. In concrete, two sheets of 9.09 wt. % and of 16.6 wt. % of the composite papers are prepared (four sheets in total), respectively. To obtain above two types of samples, we follow the following procedures.

I-1. Preparing 2 mg of the powdery semiconducting CNT (93% purity, (6,5) chirality, SouthWest NanoTechnologies Inc.) and 2 mg of SDS.

I-2. Putting the CNT and SDS into 10 ml of pure water and applying ultrasonication to them for one hour to prepare the semiconducting CNT dispersion.

II. Preparing 30 mg of the pulp materials, putting them into 15 ml of pure water, and dispersing to prepare the pulp dispersion for each composite paper.

III. Following the papermaking method as described above with the mixed dispersion made from I and II. To prepare two types of the samples with a difference CNT content, we prepare two CNT dispersions made from the process I, and divide II dispersion into 2-to-1 for the preparation of two types of mixed dispersions.

Here, the semiconducting CNT-composite paper usually shows the p-type property. To obtain a larger Seebeck effect in the semiconducting material, p-type and n-type semiconductors must be prepared and connected with alternately [1]. Therefore, we must prepare an n-type composite paper. For this, we focus on a doping technique reported in Ref. [4]. In concrete, we firstly prepare chemicals $(CH_3)_4NOH$ (the concentration: 0.1 mol/l) and $[C_2H_4O]_6$ (0.1 mol/l) as a reducing agent and a stabilizer for the CNT. Next, we drop 0.5 ml of each chemical to 1.5×6.5 cm^2 of the CNT-composite paper. Finally, we dry the composite paper, and also verify the n-type behavior.

To evaluate the Seebeck effect of the composite paper, we measure the electromotive force of the sample as a function of temperature difference in it. We provide a temperature difference to test for the both ends of the sample by using a heating device for one side of the sample. Then, we provide the temperature differences for the metallic and the semiconducting CNT-composite papers from 50 to 100 K and evaluate the thermoelectric power generation of them, respectively. After that, we prepare two

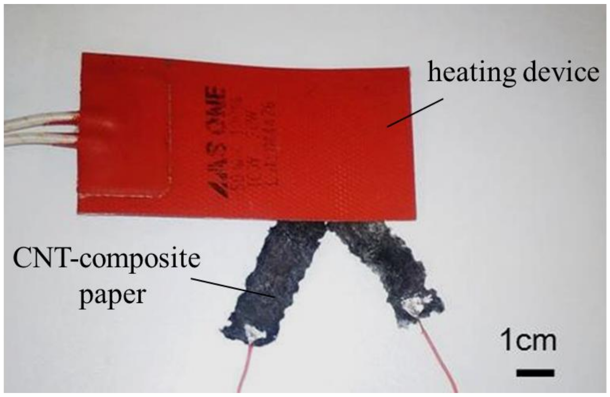

Figure 3: Actual test situation. In this case, connected two sheets of CNT-composite papers (one n-type and one p-type papers are connected in series) are heated by heating device.

pairs of the semiconducting CNT-composite papers that are constructed by connecting p- and n-type composite papers, and confirm the thermoelectric power generation of them by providing the temperature differences from 20 to 70 K. Figure 3 shows the actual circuit diagram.

3 EXPERIMENTAL RESULTS

We tested the thermoelectric power generating ability of our CNT-composite papers as described above. In the following subsections, the evaluated power generating ability of the metallic and semiconducting CNT-composite papers are described (Sec. 3.1), and the evaluation of the ability of connected numbers of the CNT-composite papers are described (Sec. 3.2).

3.1 Evaluation of Thermoelectric Power Generating Ability of Metallic and Semiconducting CNT-Composite Papers

Figure 4 shows the experimental results for the one sheet of the metallic and the semiconducting CNT-composite papers. Here, the vertical axis shows the estimated Seebeck coefficient (S [μV/K]) that is an indicator of thermoelectric power generation performance, and the horizontal one shows the temperature difference from 50 K to 100 K for the composite papers. From this result, we confirmed that the Seebeck effect was observed from both papers. Especially, a large Seebeck effect was observed from the semiconducting paper. Thus, we should choose the semiconducting papers for aiming "thermoelectric power generating papers."

3.2 Evaluation of Ability of Connected CNT-Composite Papers

Figure 5 shows the experimental results of the two types of two-sheet-connected semiconducting papers. Both types i and ii were constructed by connecting with one n-type and one p-type composite papers. The difference between them is the concentration of the contained CNTs; i.e., the type i contained 9.09 wt. % of the CNT and the ii contained 16.6 wt. %. Here, the vertical axis shows the estimated Seebeck coefficient and the horizontal one shows the temperature difference from 0 K to 50 K. From these results, the Seebeck effect was observed despite the small temperature difference. In comparison with the results of one sheet of the CNT-composite paper (Fig. 4), it is clear that there is a difference of about twice in the temperature difference of 50 K. Further, we confirmed that the type i showed good performance comparing with the ii. We considered that the amount of the contained pulp materials was effective to keep its thermal conductivity low. Therefore, we must control the CNT content, i.e., there may be an appropriate balance between amounts of the pulps and the CNTs.

Next, we connected to the above types i and ii samples in series to observe the electromotive force. The result showed that 90 μV/K of the Seebeck coefficient was

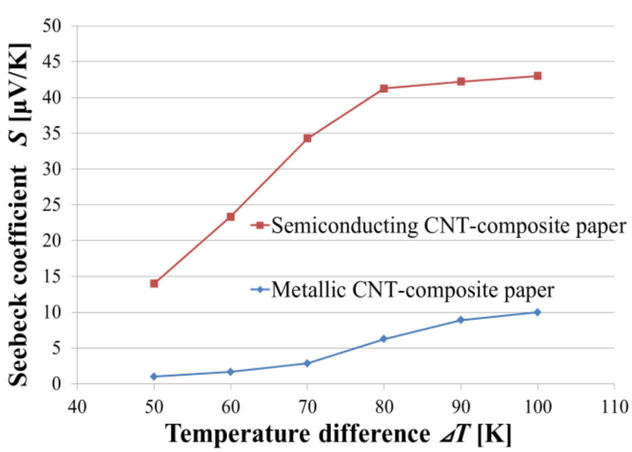

Figure 4: Experimental results of the metallic and semiconducting CNT-composite papers.

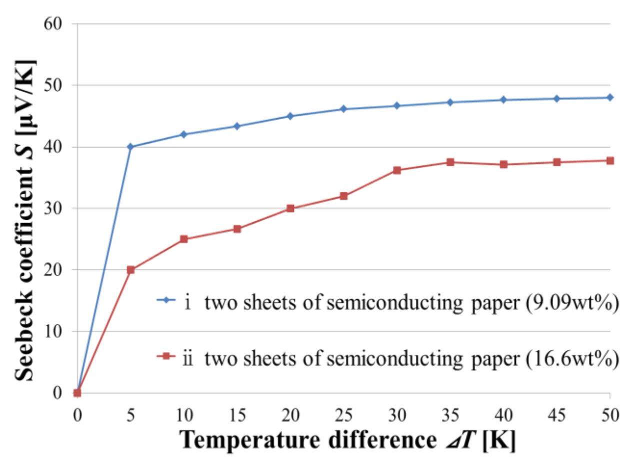

Figure 5: Experimental results of two sheets of the semiconducting CNT-composite paper.

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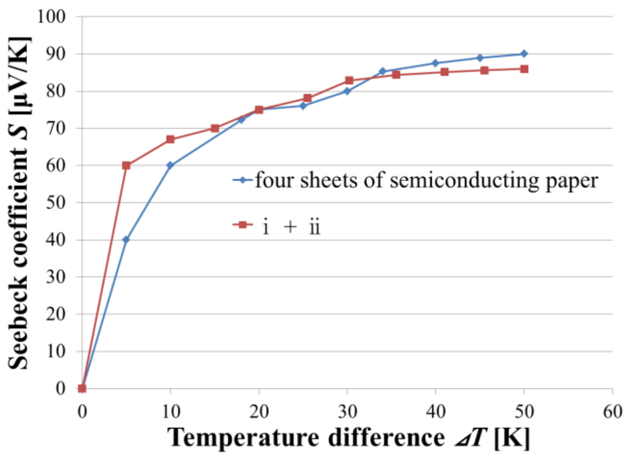

Figure 6: Experimental result of four sheets of the semiconducting CNT-composite paper and added data based on types i and ii for comparison.

obtained in a maximum. In comparison with the results of two-sheet-connected (Fig. 5), the four-sheet-connected sample showed about twice electromotive force. Here, we added the results of types i and ii mathematically to find out the improvement of performance by the number of connections (see Fig. 6).

As the results, the observed data were agreement. Therefore, the Seebeck effect using CNT-composite paper can be improved by connecting the p-type and the n-type papers simply.

4 CONCLUSIONS

In this study, we used the CNT-composite paper that a composite material of the CNT and the paper as the unique thermoelectric material, i.e., the "thermoelectric power generating paper." First, we confirmed the thermoelectric power generating ability of the metallic and the semiconducting CNT-composite papers. Then, a larger effect was observed from the semiconducting paper. Next, we prepared two types of two-sheet-connected semiconducting papers and evaluated them. As results, we found that our CNT-composite paper can be used as the "thermoelectric power generating paper." Moreover, we found that the amount of the contained pulp materials was effective to keep its thermal conductivity low for the efficient thermoelectric power generation and that the appropriate balance between amounts of the pulps and the CNTs should exist.

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