Hindawi
Journal of Nanotechnology
Volume 2019, Article ID 8385091, 6 pages
https://doi.org/10.1155/2019/8385091

*Research Article*

# Thermoelectric Effect of Buckypaper/Copper Assembly

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Received 1 June 2019; Accepted 17 September 2019; Published 13 October 2019

Academic Editor: Marco Rossi



Carbon nanotubes (CNTs) exhibit excellent electrical and thermal properties that have been used in several device assemblies, such as electrode sheets made from an aggregate of CNTs, also called as buckypaper (BP). Despite that, the properties of single CNTs are reduced when randomly assembled to form a BP. In this way, this study investigated the thermoelectric effect of a BP electrode assembled on a copper electrode with an active area of $4.0\,cm^2$. The micrographs were obtained by scanning electron microscopy and show morphology agglomerated of multiwalled CNTs, which permeated into the filter paper, forming a thickness of $67.33\,\mu m$. Moreover, *indoor/outdoor* tests were performed approaching the BP electrode from a heat source. Thus, the electrical responses in function of temperature variation show maximum thermovoltages of 9.0 mV and 40.73 mV from *indoor* and *outdoor* tests, respectively. Finally, an average Seebeck coefficient for the BP/copper electrodes array of $35.34 \pm 6.0$ mV/K was estimated from 298 to 304 K. These findings suggest that this assembly will be easily applied in thermoelectric device concepts.

## 1. Introduction

Thermoelectric technology is based on a semiconductor junction with p-type and n-type material between a hot and cold side for power conversion. In general, semiconductor materials such as Si, GaAs, and CdS show Seebeck coefficient (thermoelectric power) and photoresponse under heating [1–3]. Nowadays, the BiTe elements are used as commercial Seebeck material, and it displays a thermoelectric power of $570\,\mu V/K$ achieved with a working temperature up to 573 K in the hot side [4].

On the other hand, thermal, electrical, and optical properties of CNTs attract the attention of industry to applications in electronic devices, such as sensors [5–8], power sources [9–12], and batteries [13–15]. Many studies have shown that the one-dimensional structure of CNTs is helpful to ballistic transport, where thermal conductivity is governed by phonons and a synergetic interaction occurs between electron and phonons [16–18]. Thus, Yang et al. report that the multiwalled CNTs (MWCNTs) show an electric conductivity around $1.6 - 5 \times 10^3$ S/m at 300 K [18]. In this sense, Kim et al. show that an individual MWCNT, in the same temperature, presents a significant thermal conductivity of 3000 W/mK [19], which is much greater than copper [20]. Moreover, single MWCNT displays a thermoelectric power (TP) of $80\,\mu V/K$ [19], while for the other type, MWNTC bulk materials, the TP was obtained at a valor of 8.0 to $20\,\mu V/K$, with a temperature variation of 328 to 958 K, respectively [21].

Research has shown that thermoelectric materials and efficient designs are very important for converting waste heat into electrical energy [22]. Thermo-electrochemical cells based on BP of MWCNTs electrodes has been used in redox processes because of their high electrical conductivity and superficial area, in which the Seebeck coefficient corresponds to 1.4 mV/K [10]. Similar result was obtained in another study, but using CNT aerogel sheet as a thermoelectric material into the electrochemical cell [12]. In other aspects, different designs could be applied to improve the performance of power devices, i.e., the integration of vertically aligned MWCNT absorbers in solar thermophotovoltaic devices shows a highest conversion efficiency of 3.2%, which was three times bigger than similar devices [11]. In common with all of them was the application of BP based on random or oriented MWCNTs with/without framework support for increasing the TP. These studies clearly show that the assembly is very important in thermoelectric generations.

In our study, a thermoelectric device was designed based on the BP electrode as hot side and copper electrode as cold side, as shown in Figures 1(a)–1(c). The BP was manufactured with MWCNTs impregnated into cellulose fibers, which act as absorbers of waste heat. This BP/copper sandwich capacitor configuration was tested *indoor*/*outdoor* under variation of temperature, and a TP was measured from 298 K to 304 K.

## 2. Experimental Details

*2.1. Thermocell Manufacturing Process.* Functionalized MWCNTs with a purity of 99.80% were dispersed in isopropyl alcohol (1.0 g/L) under 40 kHz for 60 min at room temperature. After that, the alcohol was removed by filtration using filter paper (grammage of 80 g/m$^2$, diameter of 18.5 cm, and pore size of 14 $\mu$m) and kitasato flask under vacuum, as shown in Figure 2. To remove the solvent completely and obtain a dried BP, the material was placed in an oven for 1 h at 100°C.

The BP was assembled on the copper electrode and joined both with polyvinyl alcohol (PVA). Thus, the BP was configured as the positive electrode, while the copper electrode as the negative electrode with an active area of 4.0 cm$^2$. At the end, a DC voltage of 2.0 V for 30 minutes was applied in the device in order to obtain the orientation of a dipole moment in the dielectric layer between BP and copper electrodes. Before thermoelectric tests, the device was completely discharged to avoid residual voltage on the measurement records.

*2.2. Morphological Characterization and Thermoelectric Tests.* The morphology of the top view and cross-section view of BP was characterized by scanning electron microscopy (SEM) using a VEGA3 SB-TESCAN at 20 kV. The SEM micrographs were performed by secondary electron mode with work distances of 5.40 mm and 7.63 mm. For electric measurements under variation of temperature, the voltage of the thermocell was measured via two-point method by digital multimeter ET-2232 MINIPA and connected to computer via USB port. The temperatures were collected with a TD-955 infrared thermometer.

The thermoelectric tests occurred inside/outside the laboratory at room temperature without/with approach of flame as heat source, i.e., namely as *indoor*/*outdoor* tests, respectively. In the *outdoor* test, the flame was placed at a distance of 100 cm and 20 cm from the BP electrode of the thermocell. The average TP was obtained through the infrared radiation emission from a power lamp of 250 W above the BP electrode at a distance of 20 cm.

## 3. Results and Discussion

Figure 3 shows the SEM micrographs of the BP in top view and cross-section view. Random spread MWCNTs has been observed on the filter paper in Figure 3(a), where agglomerated CNTs can be seen at the top. In Figure 3(b), the CNTs permeated almost 40% (64.33 $\mu$m) of the BP with a thickness of 174.94 $\mu$m, i.e., the CNTs were impregnated into filter paper to forming a support framework. Therefore, the type of paper is an important variable that determines the final morphology obtained from BP. For instance, Reis et al. reported a BP produced on commercial paper as support, but that happened differently in our case, the CNTs were absorbed only in the surface because of the absence of porosity [23].

In the *indoor* test, the thermocell was subject to a room temperature of 30 ± 1.15°C, and it showed a thermovoltage of 7.2 to 9.0 mV, as shown in Figure 4. Note that the variation of the voltage was linearly dependent of the temperature. Moreover, when the heat source approached the front of BP electrode of the thermocell from 100 cm (i) to 20 cm (ii), then the voltage increased to approximately 4.0 mV. On the other hand, the voltage increased around 28 mV when the distance was 20 cm, but the temperature of the heat source increases from 80°C (iii) to 170°C (iv), and the voltage achieved a maximum of 40.73 mV. Similar results were reported by Kouklin et al., where the variation of the thermal radiation emitted from a heat source was correlated to peaks of the thermovoltages [24].This phenomenon is explained by high-infrared absorption capacity of the CNTs, which cause a radiation trapping with multiple internal reflections into the array [25].

Figure 5 shows thermoelectric parameters extracted from the thermocell device under room temperature (stage I) and heating (stage II and III), where in Figure 5(a), the thermovoltage as a function of the difference of temperature between the BP electrode and copper electrode ($\Delta$T in Kelvin) remained a stable level of 64 mV in stage I, when $\Delta T$ achieved a value of approximately 1.70 K, and the thermovoltage increased until 78 mV that corresponded to stage II, i.e., the infrared lamp was turned on, and the temperature on the BP electrode grew up from 300 K to 302 K, but after that saturation occurred (stage III), where the thermovoltage of 79 mV was remained constant. These results could be compared with usual materials applied as absorbers of waste heat, where a hot side of the BiTe elements was placed by Ag film, Si, and nanostructured black-Si, as shown in Table 1. Note that BP/copper assembly presents a thermovoltage higher than other materials and competitive data in other parameters.

The Seebeck coefficient or TP was calculated by the ratio $\Delta V/\Delta T$ that corresponds to the interpolated curve shown in Figure 5(b). The thermocell exhibited positive TP values dominated by p-type density carriers from BP electrode, where an average TP of 42.83 ± 4.76 mV/K and 32.84 ± 4.0 mV/K were extracted at room temperature and heating, respectively.

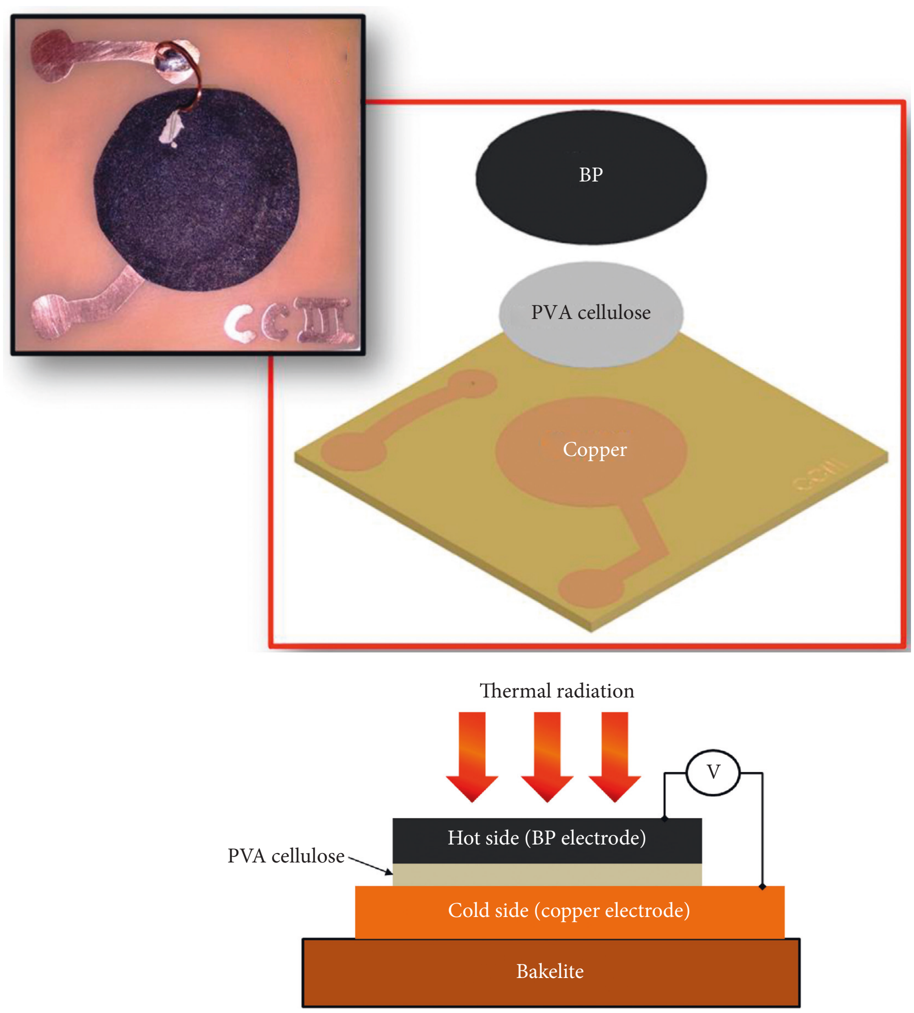



Figure 1: Thermocell designed as a sandwich capacitor, where the BP electrode can be seen in top view (a), the scheme shows the parts of device in perspective (b) and set up used in thermoelectric characterizations (c).

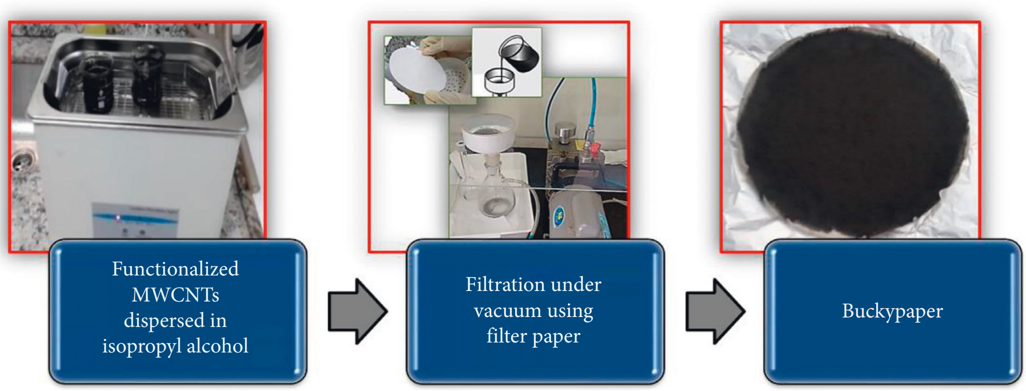
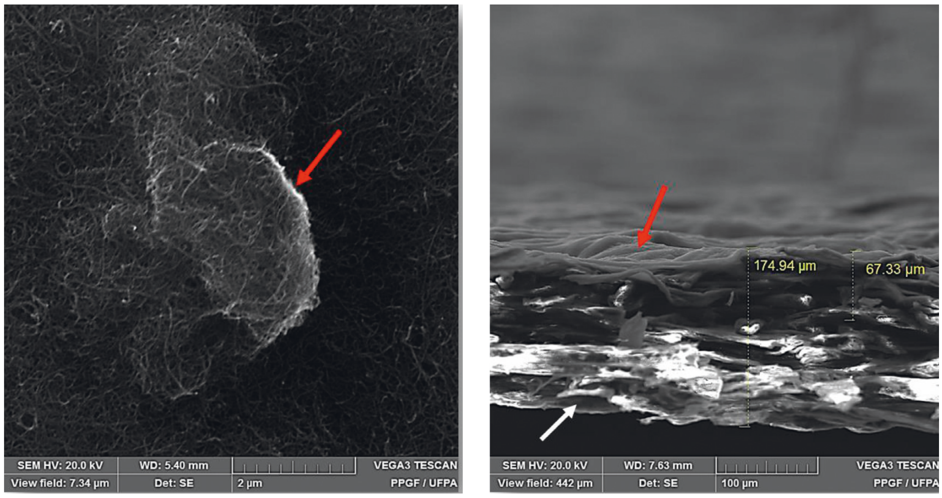



Figure 2: Manufacturing process of the BP by vacuum filtration.

These results were much greater than the TP of 1.4 mV/K obtained from thermo-electrochemical cells reported by Hu et al. [10] and Im et al. [12]. This happened because the dielectric layer of PVA-cellulose between the BP electrode and copper electrode helped to charge accumulation. Thus, the BP/copper assembly operated as a sandwich capacitor when a thermal excitation promoted the increase of the density carries and consequently the increase of the thermovoltage.




(a) (b)

FIGURE 3: SEM micrographs of the BP electrode, where the top view shows aggregated MWCNTs (a) and cross-sectional view exhibits MWCNTs (red arrow) impregnate into the cellulose of filter paper (white arrow) (b).

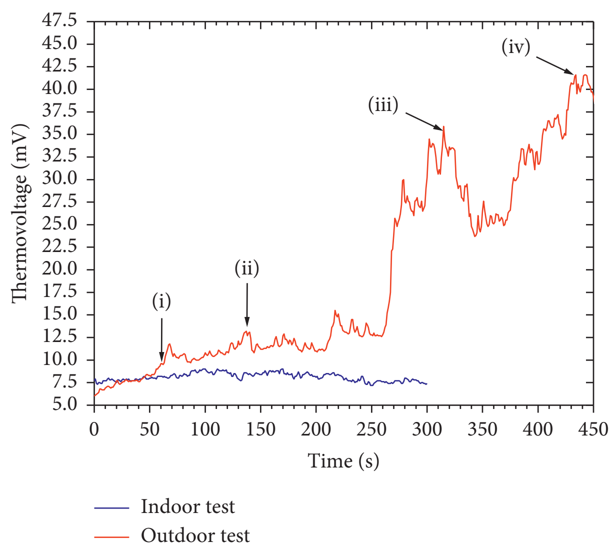
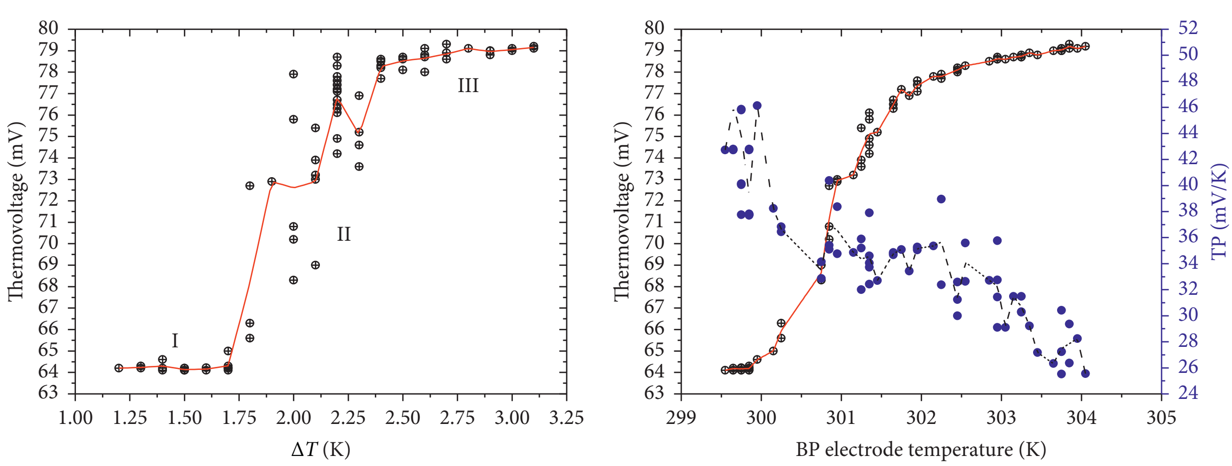



FIGURE 4: *Indoor*/*outdoor* tests show thermoelectric responses of thermocell under room temperature and heating with heat source in real conditions.




(a) (b)

FIGURE 5: Temperature dependence of voltage (a) and thermoelectric power of the thermocell (b). The values were extracted from device under room temperature and heating with infrared lamp.

Table 1: Comparison of thermoelectric properties of usual/nano materials.

| Material | $\Delta T$ (K) | Thermovoltage (mV) | TP (mV/K) |
|---|---|---|---|
| BiTe* | 120 | ~68.40 | ~0.57 |
| Black-Si** | 1.25 | 40 | 32 |
| Si** | 0.90 | 25 | 27.77 |
| Ag film** | <0.20 | <4.0 | <20 |
| This work | 3.00 | 79 | 26.33 |

*Commercial Seebeck element (TEP1-1264-1.5, Nihon Techno Ltd.). **Absorbers on hot junction of the commercial Seebeck element [4].

## 4. Conclusion

In summary, we reported the fabrication of a thermocell based on BP/copper assembly, where the BP electrode was used as an absorber of thermal radiation and a layer of PVA-cellulose as a dielectric between BP and copper electrodes. This configuration behaved as a sandwich capacitor, in which the absorber concentrated thermal energy acted as the hot side while the copper electrode was the cold side. The interesting assembly helps to pave the way for new designs of thermoelectric devices, where the carbon nanomaterials performing a double function, i.e., as absorbers of waste heat and as a charge supply layer. Therefore, the total average TP of $35.34 \pm 6.0$ mV/K was estimated from 298 to 304 K. Moreover, *indoor/outdoor* tests were performed in order to investigate the thermoelectric responses of the thermocell under controlled/real conditions and show thermovoltages of 9.0 mV at room temperature and 40.73 mV in front of the flame. Our results indicate that the BP/copper assembly could be applied in new concepts of thermoelectric devices, such as low-cost fire sensors or thermocells.

## Data Availability

Any data and information used to support the findings of this study will be provided by the corresponding author upon request.

## Conflicts of Interest

The authors declare that are no conflicts of interest regarding the publication of this paper.

## Acknowledgments

Paula F. P. Pinheiro and Luiza M. P. Ferreira would like to express heartfelt thanks to the PROPESP/UFPA (PIBIC fellowship and article charge) for providing financial support. The authors acknowledge the LABNANO-AMAZON/UFPA network for the support to the facilities used in this work.

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