Facile fabrication of paper-based flexible thermoelectric generator

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Paper, as a foldable, pollution-free, and low-cost material, has become a suitable support substrate for producing flexible thermoelectric (TE) generators to realize waste heat recycling and the application of human-powered electronic devices. We propose a facile fabrication method to modify cellulose paper with inorganic TE powders via vacuum filtration, making a modified paper that possesses good thermoelectric properties. By connecting the modified paper to copper foils, flexible paper-based TE generators (PTGs) are fabricated. The obtained PTG with three units of P–N modules can generate an output voltage of ~41.2 mV at a temperature difference of 50 K. Based on this modified paper, a thermal sensor that responds to heat sources, such as fingers, is proposed with a rapid response time of 0.25 s. This work offers a promising strategy for the simple fabrication of PTGs, paving the way for achieving the commercial application of self-powered wearable electronics.

RESULTS AND DISCUSSION

Fabrication of the generators

Figure 1a shows the fabrication process of modified cellulose papers and PTGs. The N- and P-type modified papers are prepared through the vacuum filtration method. The N-type material is Bi2Te3 doped with Se, and the P-type material is Sb2Te3 doped with Bi. First, N-type TE powder (100 mg) and sodium carboxymethyl cellulose (CMC-Na) are dispersed in 30 ml deionized water at a mass ratio of 12 to 1, and the mixture is stirred for 10 min to form an N-type TE dispersion. CMC-Na is used to enhance the stability of the TE dispersion. The dispersion is then sonicated for 40 min to reduce the particle size of the TE powder and to allow it to fully disperse. The treated dispersion is poured into a vacuum flask for suction filtration. A pump is connected to the suction bottle mouth to maintain a pressure difference. The relative pressure is ~0.06 MPa, and suction filtration is conducted for 4–5 h. The P-type TE powder is prepared with the same procedure. The experimental process of vacuum-assisted filtration has been successfully circumvent the brittleness of inorganic semiconductors to achieve flexible PTGs and demonstrate their possible application.

There are some issues, such as complicated preparation processes, high preparation costs, and poor performance in current PTGs. Therefore, it is necessary to develop more efficient and inexpensive preparation techniques to achieve the large-scale application of PTGs. In this work, we explore a simple method to modify cellulose paper and use modified paper to fabricate PTGs. In this method, cellulose paper is modified by infiltrating inorganic TE materials (doped Bi2Te3 and Sb2Te3) into a paper matrix via a vacuum-assisted filtration process. The foldable PTGs are fabricated by connecting the cut modified paper to copper foils. The obtained PTG with three units of P–N modules can generate ~41.2 mV at a temperature difference of 50 K. Furthermore, based on the modified paper, a finger touch sensor is fabricated, which can respond quickly to heat sources with a relaxation time of 0.25 s. This work demonstrates the feasibility of PTGs and thermal sensors prepared by modified cellulose paper.

INTRODUCTION

The invention of cellulose fiber-based paper has undoubtedly contributed greatly to the progress of society over thousands of years. Recently, paper has also become a popular and promising component used in flexible electronics due to its foldability, low cost, light weight, and environmental friendliness1–5. Some techniques, such as printing and magnetron sputtering, are perfectly combined with paper, making paper a substrate or technique, such as printing and magnetron sputtering, are perfectly combined with paper, making paper a substrate or

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Preparation process of flexible paper-based thermoelectric generator (PTG) and the photos display. a Schematic diagram of the fabrication process for PTGs. The N- and P-type modified papers are prepared through the vacuum filtration method, cut into small strips and connected with copper foil in an alternating sequence. b–e Photographs of the complete modified papers obtained by the vacuum filtration method (b), displaying their high flexibility (c), the small 5 mm × 20 mm strips (d), and the PTG with three units of P–N modules (e). The smallest grid point of the background grid paper represents 1 mm.

Fig. 1 Preparation process of flexible paper-based thermoelectric generator (PTG) and the photos display. a Schematic diagram of the fabrication process for PTGs. The N- and P-type modified papers are prepared through the vacuum filtration method, cut into small strips and connected with copper foil in an alternating sequence. b–e Photographs of the complete modified papers obtained by the vacuum filtration method (b), displaying their high flexibility (c), the small 5 mm × 20 mm strips (d), and the PTG with three units of P–N modules (e). The smallest grid point of the background grid paper represents 1 mm.

We prepare modified papers through the vacuum filtration method (b), with 100, 200, and 300 mg of TE powders, respectively. The modified papers are cut into identical strips with dimensions of 5 mm × 20 mm, which are shown in Fig. 1d. After this, the small strips are used as TE legs and are alternately connected to copper foils in the form of an “N–P–N–P” sequence to form a conductive path. Both sides of the obtained series of TE legs are covered with polyimide (PI) for packaging and then flattened with a pressure anvil at 10 MPa to enhance the compactness of the TE particles. After the wires are attached on the ends of the TE legs, the flexible PTG shown in Fig. 1e is finally fabricated, which is comprised of several pairs of P–N modules. This is a facile and inexpensive method for preparing flexible TE generators and can be applied on a large scale.

General characterization

The cross-sectional morphology of the modified paper was characterized by scanning electron microscopy (SEM). For comparison, Fig. 2a, b shows the cross-section SEM images of the pristine paper at scale bars of 100 and 10 μm. The inset of Fig. 2a is a photograph of filter paper used in the experiment. Figure 2c provides the cross-section micromodel, which shows that paper is composed of adjacent and interlaced cellulose fibers. Figure 2d, e shows the SEM images of the N-type modified paper at the corresponding scale. In Fig. 2d, the upper layer of the modified paper is enlarged in the insert with a scale bar of 50 μm, and the lower layer is enlarged in Fig. 2e. Through vacuum filtration, some of the particles are deposited on the surface of the paper, which forms a compact layer called the deposition layer, while some of the particles penetrate into the paper and adhere to the cellulose fibers, forming an infiltration layer. The final modified paper consists of a deposition layer and infiltration layer, and its structural model is illustrated in Fig. 2f. Due to the same treatment procedure, the sizes of the N- and P-type powders are similar (less than 10 μm). The TE grains in the deposition layer are compact and are adjacent to each other to form a conductive path. The grains that infiltrate into the paper are used as a conductive supplement, and the cellulose fiber ensures the flexibility of the modified paper.

The elemental composition of the active materials in the modified paper was characterized by transmission electron microscopy (TEM). The P-type TE material is Sb2Te3 doped with Se, and the N-type is Bi2Te3 doped with Bi. Their crystalline structures are exhibited in Fig. 2g, h, which show that Sb2Te3 and Bi2Te3 are hexagonal crystalline structures formed by stacking quintuple layers. The two quintuple layers are connected by weak van der Waals forces. Figure 2i, j are high-resolution TEM (HRTEM) images of Sb2Te3 doped with Bi and Bi2Te3 doped with Se, respectively. The corresponding fast Fourier transform (FFT) images indicate the hexagonal structure of both Sb2Te3 and Bi2Te3. Both the HRTEM and FFT images show the good crystallinity of Sb2Te3 and Bi2Te3. Figure 2k, l are the energy
Fig. 2  Microscopic characterizations of pristine and modified papers with SEM and particles with high-resolution TEM. a Cross-sectional SEM images of the pristine paper with scale bars of 100 μm and b 10 μm. The inset of a is a photograph of the filter paper used in the experiment. c Simple structural model of the filter paper with the adjacent cellulose fiber. d Cross-sectional SEM image of the N-type modified paper with a scale bar of 100 μm. The insert is an enlarged view of the deposition layer on the upper part of the modified paper, and the scale bar is 50 μm. e Enlarged view of the infiltration layer marked with an orange rectangle in (d). The TE particles are less than 10 μm. The SEM images are from the N-type modified paper. f Micromodel of the modified paper composed of a deposition layer and infiltration layer. g Crystalline structures of Sb₂Te₃ doped with Bi and h Bi₂Te₃ doped with Se. i High-resolution TEM images and the corresponding fast Fourier transform (FFT) images of Sb₂Te₃ doped with Bi and j Bi₂Te₃ doped with Se. The scale bars are 0.5 nm. k Energy dispersive spectroscopy (EDS) results of Sb₂Te₃ doped with Bi and l Bi₂Te₃ doped with Se. The atomic percentages of the corresponding elements are listed in the inserted table.
dispersive spectroscopy (EDS) results of Sb_2Te_3 and Bi_2Te_3, respectively. The atomic percentages indicate that Sb:Te:Bi is approximately 33:61:6 and Bi:Te:Se is approximately 46:50:4. The specific composition of the N- and P-type active materials has been clarified.

Performance of the generators

PTGs with 1–3 units of P–N modules are fabricated and packaged with PI. The TE performance of the PTGs was tested, as shown in Fig. 3a–c shows graphs of the open-circuit voltage of PTGs with different weight percentages of active materials versus the temperature difference. At the same weight percentage, the open-circuit voltage increases proportionally with the units of the P–N modules. The largest voltage reaches ~ 41.2 mV at a ΔT of 50 K and a weight percentage of 70%. The open-circuit voltages with different weight percentages at a ΔT of 30 K are summarized in Fig. 3d. This figure shows that as the weight percentage increases, the generated voltage increases because more active materials participate in power generation. In regard to the weight percentages at 37%, 59%, and 70%, the PTGs with three units of P–N modules generate open-circuit voltages of ~19.6 mV, ~22.3 mV and ~25 mV at a ΔT of 30 K, respectively. The Seebeck coefficient is an important parameter to characterize TE performance, which is defined as the magnitude of the generated TE voltage per degree of temperature difference. The definition can be expressed as

$$ S = \frac{dV}{dT} $$  \hspace{1cm} (1)

where S is the Seebeck coefficient and V is the TE voltage. Thus, the Seebeck coefficients of the flexible PTGs are obtained by calculating the single leg of PTGs, which are shown in Fig. 3e. For modified paper_37, modified paper_59, and modified paper_70, the average Seebeck coefficients are 112, 128, and 142 μV·K⁻¹ (absolute value), respectively. Compared to previous reports on flexible TE generators, which are listed in Table 1, the above values are impressive. Of course, the high efficiency of TE generators is not determined by a single parameter, which requires us to make further efforts to this end. Figure 3f shows the variations in the external circuit voltage and output power with current in the PTG with three units of modules. As the load resistance decreases, the current in the circuit increases, and the voltage across the resistor decreases. The value of the output power is the product of the external circuit voltage and current.

| TE materials | Method | Seebeck coefficient (μV·K⁻¹) | Reference |
|--------------|--------|-----------------------------|-----------|
| Bi₂Te₃/paper composite | Modified distributor printing technology | 60 | 10 |
| PEDOT:PSS | Screen-printing | 99 | 18 |
| PEDOT nanowires | Vacuum-assisted filtration | 25.5 | 19 |
| Bi₂Te₃ and Sb₂Te₃ modified paper | Vacuum-assisted filtration | 142 | This work |

Table 1. Comparison of the reported Seebeck coefficient of a single leg of the flexible TE devices at room temperature.
The current can be obtained by

\[ I = \frac{U_o}{R_i + R_L} \]  

(2)

where \( U_o \) is the open-circuit voltage of the TE device, \( R_i \) is the internal resistance of the PTG, and \( R_L \) is the load resistance of the circuit. The external circuit voltage \( U_e \) can be expressed as

\[ U_e = I \cdot R_L \]  

(3)

and the output power \( P \) can be expressed as

\[ P = U_e \cdot I \]  

(4)

In Fig. 3f, it can be observed that the maximum output power is \( \sim 709 \text{ pW} \) at a \( \Delta T \) of 40 K, \( \sim 351 \text{ pW} \) at a \( \Delta T \) of 30 K, and \( \sim 155 \text{ pW} \) at a \( \Delta T \) of 20 K. The biggest reason for the output power being at a low level is that the internal resistance of the device is too large, which is over 50 kΩ for a single leg in the PTG. The durability of PTGs is tested with repeated bending cycles. Figure 3g shows that the variation in internal resistance is less than 10% after 400 bending cycles with a bending angle of approximately 103°, and the Seebeck coefficient is less than 5%. The good stability and durability indicate the potential application of the modified paper in flexible heat source identification devices. Flexible PTGs can be applied to human skin for power generation using the temperature difference between the ambient air and body. Figure 3h displays the PTG attached to the wrist of a human body, which produces an open-circuit voltage of 2.38 mV at a temperature difference of \( \sim 5-6 \text{ K} \). This observation demonstrates that these PTGs have potential applications for human energy harvesting.

Flexible modified paper can also be used as a thermal sensor to achieve a rapid response to contacting a heat source. Figure 4a shows the voltage response of the flexible modified paper with a finger touch, and Fig. 4b is the enlarged view in the blue dashed box of Fig. 4a. The inset shows the test process of the sensor response. When the finger is completely pressed on one side of the paper for heating, the open-circuit voltage of the paper reaches approximately 5 mV. After 25 s, the position touched by the finger changes from one terminal of the modified paper to the other, and the polarity of the voltage alternates accordingly. The graphs depict that the voltage increases and decreases sharply with the finger touch at a frequency of approximately \( 1 \text{ s}^{-1} \), illustrating that the modified paper is sensitive to changes in external temperature. It is noted that the maximum voltage for each cycle is not consistent, which is due to the different temperature changes induced by the finger touch. From Fig. 4b, a response time \( (\tau_{\text{rec}}) \) of 0.25 s and a recovery time \( (\tau_{\text{recov}}) \) of 0.40 s are obtained. The response time is defined as the time required for the sensor to move from the baseline to 90% of its maximum voltage after finger pressing, and the recovery time is the time to move from 90% of its maximum voltage back to the baseline value after retracting the finger. Paper-based thermal sensors are expected to enable the self-powered control of wearable electronics.

In summary, N- and P-type modified paper and flexible PTGs were simply fabricated via vacuum filtration, and a high output voltage was obtained. Regarding the modified paper, some of the particles were deposited on the surface of the paper to form a deposition layer, and some of the particles penetrated into the paper to form an infiltration layer. The modified paper comprised of these two layers formed a conductive path. The TE particles were characterized by HRTEM and EDS, which showed that the specific component of the P-type TE material was SbTeBi with a ratio of approximately 33:61:6 and that the N-type TE material was BiTeSe with a ratio of approximately 46:50:4. The modified paper possessed a high Seebeck coefficient of 142 \( \mu \text{V K}^{-1} \), and PTGs with three units of P-N modules could obtain a maximum output power of \( \sim 709 \text{ pW} \) at a \( \Delta T \) of 40 K. Furthermore, based on the TE effect, a paper-based thermal sensor with a response time of 0.25 s was investigated. This work demonstrates the feasibility of PTGs and paper-based thermal sensors prepared by vacuum-assisted filtration.

**METHODS**

**Materials**

Doped Bi0.5Te0.5 (powder, 99.99%) and Sb2Te3 (powder, 99.99%) were purchased from Qijin New Material (Quanzhou, China). CMC-Na was purchased from Shandong Usolf Chemical Technology Company (Linyi, China). Medium-speed qualitative filter paper with a diameter of 9 cm was used in the experiment.

**Characterization and testing**

The SEM images were obtained by using an FEI XL30 FEG with an accelerating voltage of 20 kV. To conduct electricity, the cross-sections of the paper and TE film were covered with 20 nm of Au. To obtain an intact cross-section, the paper and paper-based TE film were broken after cooling with liquid nitrogen. The structural and compositional characterization of the samples were performed in a JEM-ARM300F equipped with EDS at an accelerating voltage of 300 kV. TEM samples were prepared by the ultrasonic processing and centrifugation of the powder samples. Then, the supernatants of the centrifuged samples were drop cast on lacey carbon films and dried naturally for TEM characterization.

A heating stage (NJW-3020) was used to heat the PTGs, and a thermocouple was used to monitor the real-time temperature. The voltage and sensor tests were carried out on an electrochemical workstation (CHI660E), and the current was measured by a picoammeter (Keithley Model 6485).

**DATA AVAILABILITY**

The datasets generated and analyzed during the current study are available from the corresponding authors upon reasonable request.
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AUTHOR CONTRIBUTIONS

X.W., Z.D., and H.L. conceived and designed the experiments. Z.D., J.F., and C.W. fabricated and measured the PTGs. H.L. C.L., X.C., and X.Y. characterized and analyzed the materials. X.W., H.B., C.W., and Y.Z. supervised the overall research. Z.D., H.L. H.B., X.W., and C.L. contributed to the writing of the paper. Z.D. and H.L. are contributed equally to the paper.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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