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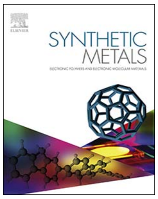

Design and fabrication of low resistance palm-power generator based on flexible thermoelectric composite film

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ABSTRACT

Human thermal energy as permanent generation energy source have been widely utilized in thermoelectric (TE) application today, especially for wearable electronics. In this work, an intrinsically flexible palm-power TE generator based on the *p*-type PEDOT:PSS-based composite films has been designed and fabricated. The combination of inorganic nano-filler and chemical treatment have been proved to be an effective strategy for improving the TE performance of PEDOT:PSS. The maximum power factor of PEDOT:PSS composite with 5% content of $(Ca_{0.85}Ag_{0.15})_3Co_4O_9$ was evaluated to be 75.2 $\mu W\,m^{-1}\,K^{-2}$ after H_2SO_4 post-treatment, which was three times higher than that of pure PEDOT:PSS. The resulting film with a good mechanical flexibility still sustained its good TE performance about 96% even after being flexed for 1000 bending cycles. Based on the parallel circuit design, the palm-power TE generator was assembled by the flexible composite films and realized a low internal resistance of 1.1 Ω and an acceptable output power of 36 nW in the palm of hand. This work may open new avenues on the design and fabrication of flexible wearable electronics for energy harvesting.

1. Introduction

With the growing demand for energy sources, more and more attention have been preoccupied with energy harvesting devices or generators [1]. Thermoelectric (TE) materials as an important part of the green energy sources have been widely concerned owing to the ability of converting natural heat sources or ubiquitous waste heat energy into useful electric energy directly [2,3]. Remarkable progress have been witnessed to pave the evolution of TE electronics to a new paradigm, wearable electronics [4]. To effectively harvest thermal source from human body for wearable electronics, TE material and generator should have good mechanical flexibility to endure the diversity actions, high output power to imply useful energy, and low internal resistance to reduce the Joule heat [5].

Calcium cobalt oxides ($Ca_3Co_4O_9$) with the conductive layer (CoO_2) and the insulating layer (Ca_2CoO_3), has been identified as one of the most promising oxide TE materials due to high natural abundance, good chemical stability, and low toxicity [6]. Single crystal $Ca_3Co_4O_9$ exhibits a high Seebeck coefficient ($\sim 130\,\mu V\,K^{-1}$) but a low electrical conductivity ($3 \sim 8\,S\,cm^{-1}$) at room temperature [7]. Interestingly, ionic substitution, such as Ag^+, which shows quite high electrical conductivity, has been regared as an effective method to enhance the electrical conductivity of $Ca_3Co_4O_9$ with maintaining a high level of Seebeck coefficient due to the strong electron correlated system [8–11]. Traditional TE generators made of rigid and brittle $Ca_3Co_4O_9$ exhibit excellent TE properties, however, they are impeded by the poor mechanical flexibility, complicated process, and cost-effectiveness, which make them not viable for wearable electronics application. Solubility and good film-forming property make organic TE material an ideal option for the fabrication of wearable TE generators. Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) due to its good film-forming property, low thermal conductivity, and high electrical conductivity has been widely concerned in TE field [12,13]. Despite all the aforementioned advantages, the mediocre Seebeck coefficient ($\sim 15\,\mu V\,K^{-1}$) of PEDOT:PSS has impeded its further application to many new TE systems [14]. Organic/inorganic composite have been proved an effective method to improve the Seebeck coefficient of PEDOT:PSS by embedding inorganic nano-filler with high Seebeck coefficient into PEDOT:PSS matrix [15–21]. Although, Liu and coworkers [22] prepared PEDOT:PSS/$Ca_3Co_4O_9$ composite with an enhanced Seebeck coefficient (24%) by drop-casting. Owing to the poor electronic transport performance of $Ca_3Co_4O_9$, the power factor of the

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composite film exhibits a decreasing trend. In view of this condition, it is a challenge to integrate the bilateral benefits of the two components and avert their defects for the development of high performance TE composites and even high output power TE generators.

In addition, the Joule heat generated by internal resistance is another key factor, which severely restricts the practical application of TE generators. Up to now, many attempts have been suggested, such as flexible design and various kinds of assembly methods, to put the high performance TE composites into practical application [4,23,24]. However, there are few reports on the circuit design to effectively reduce the internal resistance. It is noteworthy that a higher internal resistance generates a larger Joule heat for electronic devices. At present, the circuit design of TE generator still stays in multiple legs to improve the overall output power [25,26]. Kang and co-workers [27] fabricated a TE generator consisting of 32 legs arranged in two rows resulting in an enhanced output power. Although this arrangement strategy can improve the total output performance, it also increases the total resistance and Joule heat of devices, which is not conducive to the practical application. It is a key issue how to make an effective use of the existing TE materials to achieve a significant reduction in internal resistance and increase output power.

Inspired by the nature temperature of human palm that the central zone always have the higher temperature than the outer ones and the basic thinking of the parallel circuit, the goal of palm-power TE generator is expected to be achieved. In this work, the $(Ca_{1-x}Ag_x)_3Co_4O_9$ powder was synthesized by sol-gel method. The TE performance of the PEDOT:PSS/$(Ca_{1-x}Ag_x)_3Co_4O_9$ composite films with post-treatment have been systemically analyzed. The concept of parallel circuit was proposed, for the first time, to obtain a low internal resistance, which shows great potential to significantly reduce the Joule heat. Finally, a novel flexible palm-power TE generator for a glove has been designed and fabricated with an acceptable output performance.

2. Experimental

2.1. Chemicals

An aqueous PEDOT:PSS solution (Clevios PH1000) was purchased from HC Stark (Munich, Germany). Tetrahydrate calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$), hexahydrate cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), citric acid, and $AgNO_3$ were purchased from Sigma-Aldrich. Ethylene glycol (EG), Dimethyl sulfoxide (DMSO) and sulfuric acid (H_2SO_4) were obtained from Sinopharm Chemical Reagent Co., Ltd. All the above chemicals were analytical grade and used directly without further purification.

2.2. Synthesis of $(Ca_{1-x}Ag_x)_3Co_4O_9$

The $(Ca_{1-x}Ag_x)_3Co_4O_9$ power was synthesized by sol-gel method according to the previous report [28]. Firstly, $Ca(NO_3)_2{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were added in a beaker and dissolved in deionized water at 60 °C. Subsequently, the citric acid aqueous solution and 2% volume fraction ethylene glycol (EG) were added drop by drop with vigorous stirring under the condition of 80 °C, until the formation of a pink transparent sticky colloid solution. Then the colloid solution was kept into the drying oven at 120 °C for 12 h until the formation of dry gel. After that, the dried gel were grinded for half an hour and calcined in the muffle furnace at 450 °C for 6 h and then at 800 °C for 8 h. Finally, the $Ca_3Co_4O_9$ powder was obtained. $(Ca_{1-x}Ag_x)_3Co_4O_9$ (x = 0.1, 0.15, 0.2, 0.3, and 0.5 are the mass percentage of Ag) powers were obtained by Ag-substituted Ca with the specified amount of the raw materials by the same method described above. The $(Ca_{1-x}Ag_x)_3Co_4O_9$ films were obtained by compression.

2.3. Fabrication of PEDOT:PSS/$(Ca_{1-x}Ag_x)_3Co_4O_9$ composite films

Scheme 1 represents the overall fabrication procedure of $(Ca_{1-x}Ag_x)_3Co_4O_9$ powder and PEDOT:PSS/$(Ca_{1-x}Ag_x)_3Co_4O_9$ composite films with solvent post-treatment. Briefly, a 200 μL aqueous PEDOT:PSS solution was mixed with a certain $(Ca_{1-x}Ag_x)_3Co_4O_9$ suspension (0.5 mg/mL in 3.0 mL DMF) and sonicated for 1.0 h before vacuum filtration through porous PVDF membrane (pore size: 0.45 μm). The as-prepared films on PVDF membrane were immersed into water bath for 20 min and dropped down automatically from PVDF surface. The obtained films were transferred to a glass or PET substrate. Furthermore, the solvent (H_2SO_4 or DMSO) post-treatment were performed by covering the whole film with a fluid H_2SO_4 or DMSO solution for 15 min at room temperature (25 °C). Finally, the PEDOT:PSS/$(Ca_{1-x}Ag_x)_3Co_4O_9$ composite films were washed with deionized water and dried in vacuum at 80 °C for 30 min and 120 °C for 15 min for further use. All the samples were tailored into the required size ($12 \times 5\ mm^2$) for TE measurement.

2.4. Fabrication of palm-power thermoelectric generator

The optimized composite films with the maximum output performance were transferred to PET substrate and directly used to fabricate the palm-power TE generator by connecting the edge of the composite film with copper wires and silver paint. For comparison, another palm-power TE generator was fabricated by pure PEDOT:PSS film based on the method described above. Finally, the as-prepared flexible palm-power TE generator was fixed to the palm position of a glove by silver paint for practical application.

2.5. Characterization and measurement

X-ray diffraction (XRD) patterns were carried out by DX–2700 B X-ray diffractometer (Dandong Haoyuan Inc.) with Cu-Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA between 10° and 80° at a scanning speed of 2° min^{-1}. Raman spectra were analyzed by a micro-Raman spectrometer (Renishaw, InVia Microscope) equipped with a 532 nm He-Ne laser. X-ray photoelectron spectroscopy (XPS) were carried out by Thermo ESCALAB 250Xi (Thermo Scientific, Waltham, MA, USA). The electrical conductivity were measured by a standard four-point-probe technique with a Keithley 2700 by depositing four copper lines on the surface of the films with silver paint. The Seebeck coefficient were calculated by $S = -\Delta V/\Delta T$, where ΔV is the TE voltage gradient in-plane detected by Keithley 2700 after the establishment of a temperature gradient (ΔT) induced by an ohm resistive heater at the edge of the composite films.

3. Results and discussion

Fig. 1 presents the XRD spectra of $(Ca_{1-x}Ag_x)_3Co_4O_9$ powder with the different contents of Ag. One can see that there is no other diffraction peak except for the standard phase of $Ca_3Co_4O_9$ (JCPDS # 23-0110) and the second phase of Ag ($x \geq 0.15$) (JCPDS # 04-0783) in Fig. 1. The spectra of $(Ca_{1-x}Ag_x)_3Co_4O_9$ exhibit similar profiles compared with that of pure $Ca_3Co_4O_9$, indicating that the introduction of Ag does not change the crystal structure of $Ca_3Co_4O_9$.

Fig. 2 demonstrates the TE properties of $(Ca_{1-x}Ag_x)_3Co_4O_9$ depending on the contents of Ag. The variation in the TE properties of $(Ca_{1-x}Ag_x)_3Co_4O_9$ can be divided into three stages. At the first stage ($x \leq 0.1$), the electrical conductivity increased about one times higher than that of $Ca_3Co_4O_9$. It suggests that the univalent Ag^+ substitute bivalent Ca^{2+} is bound to make the hopping conduction towards Co^{3+}—O—Co^{4+} chains, which may lead to electrical property transformation [8]. While the Seebeck coefficient showed a tiny decrease from 116 to 101 μV K^{-1}. For the second stage ($0.1 < x < 0.2$), a small amount of Ag as second phase located at grain boundaries of $Ca_3Co_4O_9$ were beneficial for the improvement of Seebeck coefficient. These results indicate that the metallic Ag phase was well compatible with the $Ca_3Co_4O_9$ matrix, which was consistent with the previous report [29].