CuI/Nylon Membrane Hybrid Film with Large Seebeck Effect

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(Received 30 August 2021; accepted 27 October 2021; published online 27 November 2021)

Room-temperature thermoelectric materials are important for converting heat into electrical energy. As a wide-bandgap semiconductor material, CuI has the characteristics of non-toxicity, low cost, and environmental friendliness. In this work, CuI powder was synthesized by a wet chemical method, then CuI film was formed by vacuum assisted filtration of the CuI powder on a porous nylon membrane, followed by hot pressing. The film exhibits a large Seebeck coefficient of 600 $\mu V \cdot K^{-1}$ at room temperature. In addition, the film also shows good flexibility (∼95% retention of the electrical conductivity after being bent along a rod with a radius of 4 mm for 1000 times). A finger touch test on a single-leg TE module indicates that a voltage of 0.9 mV was immediately generated within 0.5 s from a temperature difference of 4 K between a finger and the environment, suggesting the potential application in wearable thermal sensors.

DOI: 10.1088/0256-307X/38/12/126701

With the progress of human society and the development of science and technology, the demands of energy are increasing rapidly. However, reserves of fossil fuels, such as coal and oil, are progressively decreasing, and the overuse of fossil fuels has caused serious environmental problems. Thermoelectric (TE) materials use Seebeck effect to convert heat into electrical energy. This kind of energy is clean and is promising for relieving the pressure caused by energy crisis.[1] Up to date, the markets of wearable electronic devices and sensors are fast increasing. Hence, flexible and environmental friendly power generators have attracted increasing attention. Flexible TE generator (f-TEG) can directly convert human body heat into electrical energy for powering wearable electronic devices.[2] Good f-TEG requires flexible materials with good TE properties. Performance of TE materials is evaluated by a dimensionless figure of merit, ZT. ZT is equal to $S^2\sigma T\kappa^{-1}$, with S being the Seebeck coefficient, σ the electrical conductivity, T the absolute temperature, and κ the total thermal conductivity. $S^2\sigma$ is called the power factor (PF).

Recently, considering that inorganic TE materials have high PF values, forming inorganic TE film on flexible substrate, such as polyimide (PI), poly(vinylidene fluoride) (PVDF), polyethersulfone (PES), paper, has attracted increasing attention.[3–8] For example, layer-structured Bi_2Te_3 was deposited on a carbon nanotube scaffold by magnetron sputtering, and the composite film showed a PF of ∼1550 $\mu W \cdot m^{-1} \cdot K^{-2}$ (corresponding ZT ∼ 0.89) at room temperature (RT).[3] In addition, a $Bi_{0.4}Sb_{1.6}Te_3$/Te composite film was prepared on PI by screen printing, cold pressing, and sintering at 450 ℃ for 45 min, and the film exhibited a PF of ∼3000 $\mu W \cdot m^{-1} \cdot K^{-2}$ and a ZT of ∼1 at RT.[4] However, since Te is toxic and scarce, it is very desirable to explore low-cost and environmental friendly inorganic TE materials near RT.

Copper iodide (CuI) is an environmentally friendly and stable solid material, which contains naturally abundant and nontoxic elements. The heavy element iodine leads to a low thermal conductivity, which is essential for a good TE performance. Crystalline state of CuI has three structure phases α, β and γ with different thermal stabilities.[9] The cubic α phase (above 673 K) and hexagonal β phase (above 643 K and below 673 K) are both ionic conductors. The γ phase at RT (or below 643 K) is a p-type semiconductor with a bandgap of 3.1 eV.[10] Previous research on CuI mainly focused on its electronic and optoelectronic applications.[11–14] However, it is reported recently that γ-CuI has high TE performance at RT,[15] which is considered to be a room-temperature TE material with great potential and valuable applications. First-principles calculations show that a typical Seebeck coefficient of γ-CuI is 237 $\mu V \cdot K^{-1}$.[16] In the last decade, many research groups have prepared this

Supported by the International Scientific and Technological Innovation Cooperation Project between the Governments of Key National R&D Program of China (Grant No. 2018YFE0111500), and the National Natural Science Foundation of China (Grant No. 51972234).

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material with different methods and studied its TE performance.[17–22] For example, CuI films were deposited on flexible polyethylene terephthalate (PET) substrates by reactive sputtering and the films showed a ZT of ∼0.21 at RT.[17] In addition, CuI films were also synthesized on flexible and transparent PET substrates by a successive ionic layer adsorption and reaction (SILAR) method and the films exhibited a PF of ∼66.1 μW·m^{-1}·K^{-2}.[18] However, these methods such as sputtering, pulsed laser deposition and SILAR are complicated and expensive.

Recently, our group[23] has developed a facile method to fabricate a flexible Ag_2Se film on nylon membrane: Ag_2Se nanowires were wet chemically synthesized at RT, then the Ag_2Se film was formed on nylon membrane by vacuum filtration and followed by hot pressing (200 ℃, 1 MPa, 30 min). An optimal Ag_2Se film exhibited a PF of ∼987.4 μW·m^{-1}·K^{-2} (ZT ∼ 0.5) at RT. Later, a series of research works on improving the PF were carried out.[24–27] In the present work, we prepare CuI film on nylon membrane by a similar method reported in Ref. [23] and the TE property and flexibility of the film are studied.

Experimental Method. All the raw materials including copper chloride dihydrate ($CuCl_2·2H_2O$), ethanol, ethylene glycol (EG), iodine (I_2), and sodium hydroxide (NaOH) were bought from Sinopharm Chemical Reagent Co, Ltd, China.

Cu powder was synthesized by a simple method: proper amount of $CuCl_2·2H_2O$ was dissolved in 40 ml EG, then proper amount of NaOH was dissolved in 40 ml EG. The solution of NaOH was added to the $CuCl_2$ solution with stirring for 30 min at RT to obtain a mixed solution. The mixed solution was put in a home microwave oven with 700 W power for 8 min. After the reaction, the resulting product was washed with ionized water and ethanol for several times.

The prepared Cu powder was dispersed in 100 ml ethanol, and proper amount of I_2 (with Cu/I molar ratio of 1 : 1) was slowly dissolved in the dispersion with stirring for 4 h at RT. The product (CuI powder) was washed with ionized water and ethanol for several times.

The prepared CuI powder was ultrasonically dispersed in ethanol for 10 min, then deposited on a porous nylon membrane via vacuum-assisted filtration. The as-prepared film was dried in a vacuum for 24 h at 60 ℃ and then hot-pressed at 230 ℃ and 1 MPa for 30 min. Figure 1 shows the schematic diagram of the preparation process of the CuI film. For simplicity, the hot-pressed film was named as the HP film.

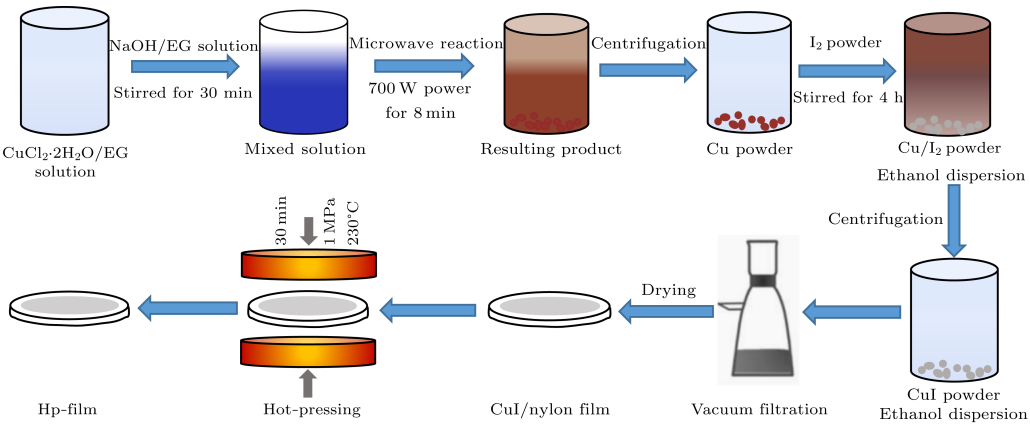

Fig. 1. Schematic diagram of the preparation process of the CuI film.

To characterize the crystallinity and phase composition of the CuI films, x-ray diffraction (XRD) (Bruker D8 Advance) measurements were performed with K_α radiation. All XRD measurements were recorded in the 2θ range of 10°–90° at a scanning speed of 5°/min. Scanning electron microscope was used to examine the samples. The temperature dependence of the Seebeck coefficient and electrical conductivity of the sample was examined by the TE material testing system (Cryoall CTA-3/500). The flexibility of the CuI film was tested by measuring the electrical conductivity after bending the film along a rod with a radius of 4 mm for different times.

A flexible single-leg TE module was fabricated by firstly sticking a strip (20 mm × 5 mm) of the CuI film on polyimide (PI) with a double faced adhesive tape, then Ag paste (SPI 04998-AB) was painted on two ends of the strip to connect with conducting wires. A finger touch test on a single-leg TE module was tested by a self-made experimental instrument.

Results and Discussion. Figure 2(a) shows the XRD patterns of the prepared CuI powder and the HP film. All the diffraction peaks of the CuI powder are consistent with those of γ-CuI (JCPDS No. 06-0246), and no other impurity peaks are detected. It is seen from Fig. 2(a) that (111), (220) and (311) plane peaks are strong, suggesting that the CuI powder has good crystallinity. The (111) plane peak is the strongest

one, maybe because the energy along (111) is lower than that along any other orientations[28,29] and the epitaxial growth of the γ-CuI layer is led by the iodination of the (111) plane of Cu particles.[30] XRD pattern of the HP film shows that all the diffraction peaks can be indexed to the γ-CuI (JCPDS No. 06-0246) without any impurity peaks. The (220) and (311) plane peaks become stronger compared with those of CuI powder, implying that the crystallinity of the CuI becomes better after hot pressing.

Figure 2(b) shows that the size of the CuI powder is about 500–700 nm. The size and morphology of the CuI powder are similar to those of Cu particles (see the SEM image in Fig. S1 in the Supplementary Material). Figure 2(c) shows a typical SEM image of the HP film. The film is porous, indicating that it is not well sintered. The cross section SEM image of the HP film is displayed in Fig. S2, which indicates that the thickness of the HP film is ∼30 μm.

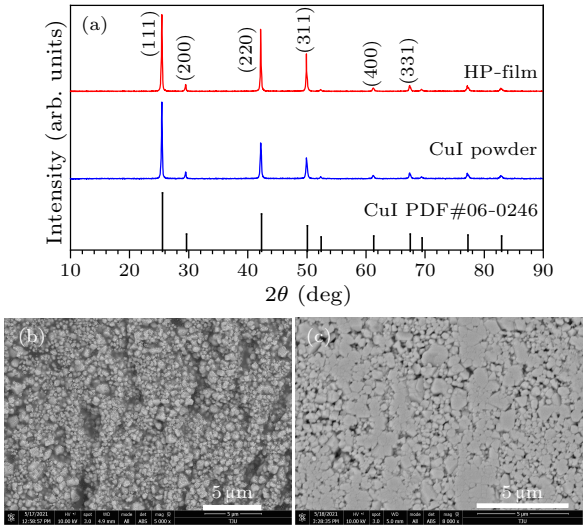

Fig. 2. (a) XRD patterns of the CuI powder and the HP film, and the SEM images of (b) the CuI powder and (c) the HP film.

The TE performance of the HP film measured from 300 to 450 K is shown in Fig. 3(a). The Seebeck coefficient of the HP film at 300 K is about 600 μV·K^{-1}, indicating that the film is p-type conduction. The first principles studies have investigated the possible formation of native defects, including vacancy, interstitial, and antisite of both Cu and I ions.[31–33] It is proposed that Cu vacancy (V_{Cu}) is the most easily occurring defect because of its low formation energy compared to the formation energies of other possible defects. It can be deduced from the p-type conductivity that the γ-CuI film was slightly copper-deficient, because V_{Cu} has been reported to be the main acceptors in p-type γ-CuI ($V_{Cu} \rightarrow V_{Cu}^{-} + h^{+}$). Here, the HP film has a large Seebeck coefficient, maybe because the single type of carrier (hole) in γ-CuI is favorable for a large Seebeck coefficient.[2] The Seebeck coefficient increases very gently with increasing temperature up to ∼390 K, then it increases quickly, and above 410 K it rapidly increases to 2694.1 μV·K^{-1} at 430 K. After 430 K, it rapidly drops to −639.1 μV·K^{-1} when the temperature is about 450 K. However, the electrical conductivity of the HP film increases steadily when the temperature increases from 300 to 340 K, and then it remains unchanged until the temperature is ∼360 K. Above 360 K, the electrical conductivity rapidly decreases to 0.14 S/cm when the temperature is about 410 K, and then it changes very little. In the film, a crossover from semiconducting to metallic behavior of conduction with increasing temperature can be found. In addition, it is indicated that the changeable temperature makes changes in the defect chemistry, leading to changes in the electrical properties. The high temperature (above 360 K) partially makes the lattice iodine release to the atmosphere, forming a donor type vacancy in the compound. Such donor-type vacancies compensate for the V_{Cu} and therefore reduce the number of holes in the material, making the film have less electrical conductivity and resulting in a large value of the Seebeck coefficient.[21] The change in carrier density also influences the electrical conductivity. Beyond 360 K, the carrier density slightly decreases due to film oxidation and deiodination, which also reduces the electrical conductivity of the film. Because the conductivity of the film is too low (it should be due to the film with high porosity), the PF is low and its change tendency with temperature is similar to that of the electrical conductivity.

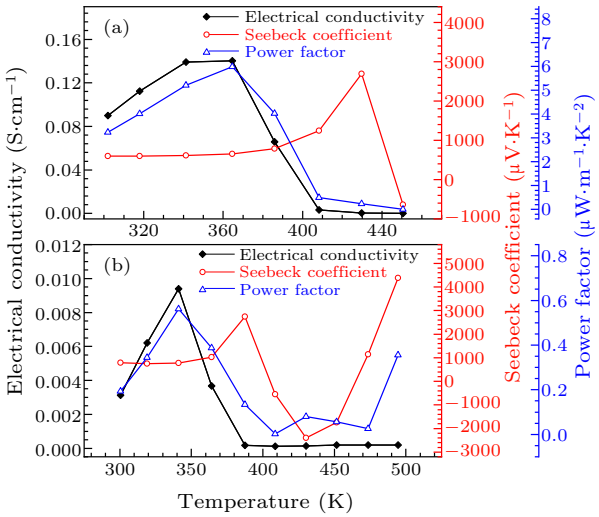

Fig. 3. Temperature dependence of electrical conductivity, Seebeck coefficient, and power factor of the HP film: (a) first test, (b) second test.

It is known from Ref. [8] that CuI exhibits p-type conduction below 643 K, namely, its Seebeck coefficient should be positive. However, in the present work, the Seebeck coefficient is negative when the temperature is above ∼445 K. To prove that this phenomenon is not accidental, TE performance test was repeated

on the film just tested, and the test temperature was increased up to 500 K.

Figure 3(b) shows the second test result from 300 to 500 K. It is seen from Fig. 3(b) that the Seebeck coefficient of the HP film at RT is increased to ~785.6 $\mu V \cdot K^{-1}$. In the temperature range of 300–430 K, the curve of S–T is similar to that of the first test, only the transition temperature of change tendency shifts from 430 K to ~385 K, and the absolute Seebeck coefficient values all become larger. It is clear that the Seebeck coefficient changes from positive to negative at ~405 K, which suggests that the first test result is not accidental. More interestingly, the Seebeck coefficient of the film starts to increase again when the temperature is above 430 K, and it changes from negative to positive again when the temperature further increases, indicating that the film can change the conduction type from p-type to n-type and then to p-type again in the temperature range. The reasons for this strange phenomenon can be considered that, due to the low formation energy of CuI crystal lattice (common problem for metal halides),[34] the CuI film may undergo iodine loss during the measurement (the temperature being elevated), and the iodine becomes vapor. The porous film will promote the iodine loss, resulting in a low electrical conductivity and weird Seebeck coefficient versus temperature behavior. In order to improve the compactness, the possible way is to synthesize smaller sized CuI particles and then hot pressing, which will be our future work.

Table 1 lists the TE properties of some reported CuI materials at RT. Because the film with extremely low electrical conductivity at RT, its PF is too low to be used for power generation; however, its Seebeck coefficient at RT is very large, which is only second to that (620 $\mu V \cdot K^{-1}$) of the bulk CuI material reported in Ref. [20].

Table 1. TE properties of the present film and some reported CuI materials at RT.

Materials	Synthesis method	PF ($\mu W \cdot m^{-1} \cdot K^{-2}$)	S ($\mu V \cdot K^{-1}$)	σ (S/cm)	References
CuI film/PET	Reactive sputtering	375	155	156.1	[17]
CuI film/PET	SILAR	30.4	85	42	[18]
CuI film/glass	Ion beam sputtering	153.8	246.7	21.9	[19]
CuI bulk	Annealing	30	620	0.75	[20]
CuI bulk	Thermal annealing	70	431	3.7	[22]
CuI film/Polyimide	Magnetron sputtering	470	206	110	[35]
CuI film/nylon	Hot pressing	3.03	600	0.09	This work

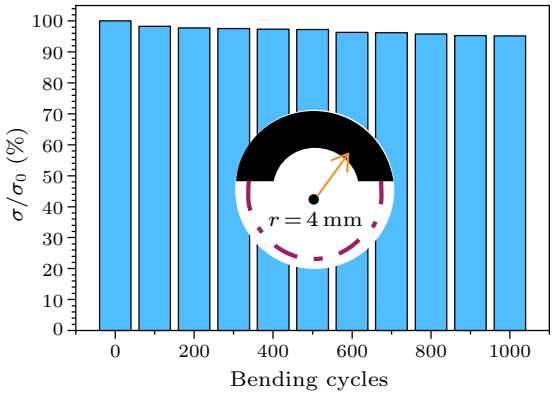

Fig. 4. Flexibility test result of the HP film (bending times dependence of change ratio of the electrical conductivity).

In addition to the TE property, the flexibility of the film is another important factor for practical wearable applications. Figure 4 shows the flexibility test results of the HP film by being bent along a rod with a radius of 4 mm for different cycles. By measuring the initial electrical conductivity (σ_0) and the electrical conductivity (σ) of the HP film after bending, the flexibility of the HP film is evaluated by the ratio of σ/σ_0. It is seen from Fig. 4 that after being bent for 1000 times, the electrical conductivity of the HP film decreases by ~5%, indicating that the HP film has good flexibility, which should be ascribed to the excellent flexibility of the nylon membrane and good combination between the CuI film and nylon membrane.

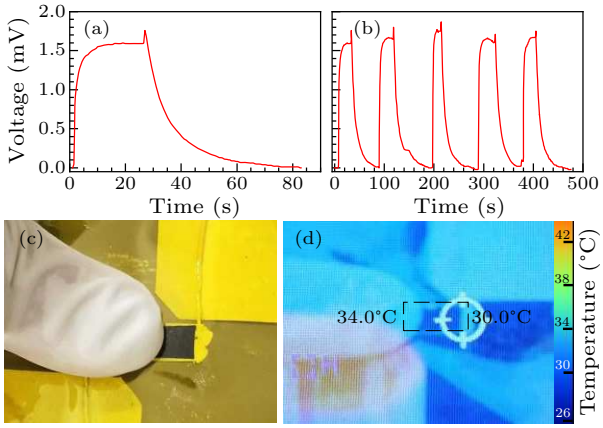

Fig. 5. A finger touch voltage test on a single-leg TE module: (a) one cycle and (b) multiple cycles. (c) A digital photo of a finger touch on a single-leg TE module. (d) An infrared thermal image corresponding to (c), showing a temperature difference of 4 K between the finger and the environment.

A single-leg TE module was fabricated with the film after being stored in a drying cabinet (20–50 RH%) for one month. Figures 5(a) and 5(b) shows a finger touch test on the single-leg TE module for one cycle and multiple cycles, respectively. Figure 5(c) is

a digital photo of a finger touching on one end of the single-leg TE module. In the test, a temperature difference between the finger and the environment (room temperature ∼30 ℃) was 4 K, as shown by an infrared thermal image [Fig. 5(d)]. It is seen from Fig. 5(a) that when the finger touched one end of the single-leg TE module, a voltage of 0.9 mV was immediately generated within 0.5 s, and the voltage reaches a maximum value of 1.6 mV after about 10 s. The Seebeck coefficient of 400 $\mu V \cdot K^{-1}$ can be calculated from the formula $S = V/\Delta T$. Obviously, this Seebeck coefficient is smaller than that shown in Fig. 3. This is mainly because the film used for fabricating the module had been stored in a drying cabinet (∼50 RH%) without being encapsulated for one month, implying that the film sample is not so stable in air, especially in humid air. Because the CuI film is porous with numerous open pores, the pores can accommodate moisture and will promote the iodine loss, resulting in the CuI film to be not very stable. Hence, the module must be well packaged before it is put into application.

The voltage quickly decreases when the finger moves away from the module and after about 48 s, it is close to 0 V. As shown in Fig. 5(b), the peak voltage value for each touch is somewhat different, which should be because the contact between the finger and film for each touch is not the same. In addition, interestingly, in each cycle, before the voltage is going to drop, it always increases slightly and then decreases markedly. This should be because the contact between the finger and the film enhances somewhat before the finger moves away. This test shows that the HP film has the potential application in wearable thermal sensors.

In summary, we have reported a method to prepare flexible CuI film on nylon membrane. The film exhibits a large Seebeck coefficient of 600 $\mu V \cdot K^{-1}$ and a low electrical conductivity of 0.09 S/cm. In addition, the film has good flexibility (∼95% retention of the electrical conductivity after being bent along a rod with a radius of 4 mm for 1000 times). A single-leg TE module has been fabricated with the film, and it can immediately generate a voltage of 0.9 mV within 0.5 s from a temperature difference of 4 K between a finger and the environment, and the maximum voltage is 1.6 mV. The large Seebeck coefficient, low-cost and flexible TE film shows great potential applications in wearable thermal sensors.

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Supplementary Material for "CuI/Nylon Membrane Hybrid Film with Large Seebeck Effect"

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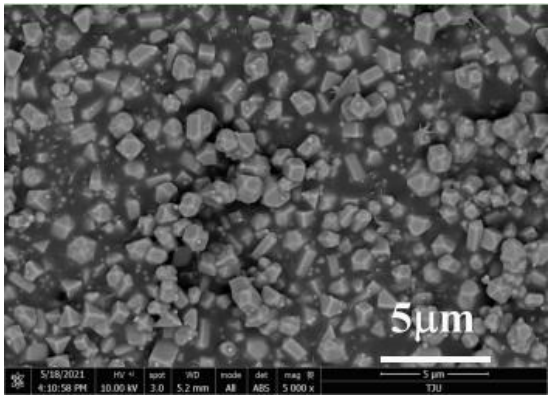

Figure S1.SEM image of the Cu powder.

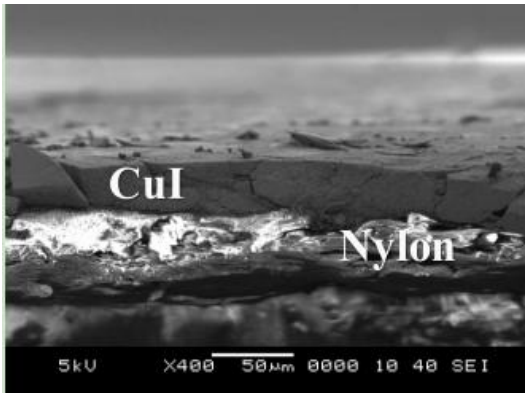

Figure S2. SEM image of the cross section of the HP-film.