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ARTICLE TYPE

Preparation of bulk AgNWs/PEDOT:PSS composites: New model towards high-performance bulk organic thermoelectric materials.

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A facile and effective approach is demonstrated to prepare high-performance bulk AgNWs/PEDOT:PSSthermoelectric composites. The thermoelectric properties of the samples with different AgNWs contents are investigated in detail. The results show that well-dispersed AgNWs the bulk PEDOT:PSS can give rise to a much higher electrical conductivity without a noticeabledecrease inSeebeck coefficient or increase inthermal conductivity, which suggests the achievement of decoupling and optimizing the electrical conductivity and Seebeck

coefficient. Consequently, the maximum ZT is observed to be 340% larger than that of pure PEDOT:PSS sample. Our work clearly proves that the introduction of AgNWs is a promisingmodel to significantly improve the thermoelectric properties of bulk organic-based TEmaterials.

15 Introduction

Thermoelectric (TE) material, a new type environmental-friendly material, which can convert waste heat into the electric energy, is now gathering people's attention.^{1, 2}The efficiency of TE materials is determined by the ZT value, a dimensionless figure ²⁰ of merit defined by the Eq.1:

$$ZT = \frac{S\sigma^2}{\kappa}T(1)$$

where S refers to the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T refers to the absolute temperature. Obviously, to gain a high ZT merit, a high ²⁵ electrical conductivity, Seebeck coefficientand low thermal conductivity are required.Unfortunately, many widely-used inorganic TE materials suffer from the inverse relationship between S and σ , which limits the further increase in power factor.³ Moreover, the long-term and painful fabrication process

with rare and expensive raw materialsalso exert negative impact on their large-scale production and applications.

Conducting polymers such as polyaniline, polythiophene and theirderivatives have exhibited great potential as highperformance TE materialsdue toextremely low thermal ³⁵ conductivity (varies between 0.2 and 0.7Wm⁻¹K⁻¹),easy synthesis and low cost.⁴⁻⁷ Among them, poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has the advantage of good processability, high stabilityand relativelyexcellentTE properties. Liu *et al.* reported a ZT=1×10⁻²

- ⁴⁰ for the DMSO (dimethylsulfoxide) doped PEDOT:PSS film.⁸ Kim *et al.* reported an extremely-high ZT=0.42 for PEDOT:PSS thin film, which is the highest reported value for organic TE materials.⁹Bubnova*et al.* successfully reported PEDOT:PSS/Tos film with a high ZT of 0.25.⁴Du *et al.* investigated a high ⁴⁵ electrical conductivity of 1295.21 Scm⁻¹ for
- $_{45}$ electrical conductivity of 1295.21 Scm for $Bi_{0.5}Sb_{1.5}Te_3/PEDOT:PSS$ film.¹⁰However, most of the above

studies about PEDOT:PSS focus on thin films, not bulk materials. It is true that in recent studies, film TE materials tend to show greater performance than bulk TE materials (both organic and ⁵⁰ inorganic) because thin films are easier to achieve special structures to control the transports of phonons and electrons.¹¹⁻ ¹³Especially for the organic TE materials, ordered structures will facilitate the electrical transports and exhibit better electrical

- properties.^{8, 14-16}However, the problem is that many micro TE ⁵⁵ devices composed of thin films are generally difficult to fabricate and design. Many of themcannot create enough temperature difference across thin film of a few µm thick to convert energy
- thus still are invalid to the large-scale commercial applications.¹⁷⁻ ²⁰Although Bulk TE materials now suffer from comparable low 60 performance, there are plenty of rooms for them to make further improvement. Therefore, despite a high ZT has been obtained in thin film thermoelectric material, bulk TE materials which is compatible with commercially available TE devices will still be the major trend. Recently, Jiang et al.andWang et al.reported the 65 syntheses of bulk PEDOT:PSS TE materials, but the bulk PEDOT:PSS suffered from relatively lower electrical conductivity compared to the thin films.^{7, 21}The thermoelectric properties of bulk PEDOT:PSS TE materials areby far lower than that of thin films. Furthermore, for many organic-based 70 composites TE materials, the enhancement in electrical conductivity will also pay for the price of lower Seebeck coefficient at the meantime.²¹⁻²³All these problems have significantly restricted the application of organic TE materials. For this sake, aneffective way for fabricating the high-75 performance bulk PEDOT:PSS-basedorganic TE materials has been developed by incorporatinginorganic nanoparticles, nanotube or nanowire into a conducting polymermatrix.
- Single-walled carbon nanotubes (SWCNT) has been reported by Moriarty*et al.*to be very helpful for promoting the electrical ⁸⁰ properties of PEDOT:PSS.²⁴Recently Coates *et al.*found Te

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nanowires/PEDOT:PSS film could exhibit higher electrical conductivity, Seebeck coefficientand a lower thermal conductivity than pure PEDOT:PSS. This unusual electrical behavior shows that low dimensional nanocrystal/polymer system can arbitic unique apportunity to aptimize 7T via molecular and

- ⁵ can exhibit unique opportunity to optimize ZT via molecular and interfacial design in ways that impossible in many classical systems.³Some newly raised research works have also demonstrated that nano-sized silver can obviouslyenhancethe electrical conductivity of both organic and inorganic materials.²¹
- ¹⁰ ^{23, 25, 26}Additionally, it has been proved that lower dimensional materials tend to achieve better TE performanceover thehigher dimensional materials mainly because the nanoscale materials canincrease the phonon scatter effect so that to suppress the thermal conductivity, thus a higher ZT value.^{3,5, 25, 27-29} Silver
- ¹⁵ nano-wires (AgNWs) as a typical one-dimensional nano-sized material, with higher electrical conductivity than SWCNT and many metals, is expected to greatly enhance the electrical properties of the organic TE materials without increasing the thermal conductivity at the meantime. Furthermore, AgNWs also
- ²⁰ have the advantage of easy synthesis, controllable aspect ratio and good dispersion in matrix. So it seems that AgNWsis a very promising choice tooptimize bothof the electrical properties and thermal conductivity of bulk PEDOT:PSS.

In this work, we propose a facile method to fabricate 25 AgNWs/PEDOT:PSS bulk TE material for the first time. The asprepared AgNWs/PEDOT:PSS composites powders were synthesized by cryogenic grinding (CG) and then consolidated by a Spark Plasma Sintering (SPS) system. The TE properties of all samples were investigated and the results show that samples well

³⁰ dispersed with AgNWs exhibited a much higher electrical conductivity than the pure bulk PEDOT:PSS, and consequently the maximum ZT value of AgNWs-dispersed PEDOT:PSS composites was found to achieve a four-times enhancement without sacrificing the Seebeck coefficient and thermal ³⁵ conductivity. This indicates the addition of AgNWs is an ideal way towards the high-performance bulk PEDOT:PSS TE materials.

Experimental section

Preparation of the AgNWs

⁴⁰ All chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd and used without any purification.

Firstly, 10ml ethylene glycol (EG) dispersed with 425.7mg Polyvinylpyrrolidone (PVP,K-30) was prepared and then 7mg NaClwas addedinto the mixed solution. Secondly, the solution

- ⁴⁵ was poured into a three-necked round flask and heated at 170°C. Then 5ml EG dispersed with AgNO₃(108.7mg) was added into the solution by an injection pump at a rate of 5ml/h. After that, the solution was heated for 1.5h with magnetic stirring until the color shifted to opaque gray, indicating the presence of AgNWs.²⁵
- ⁵⁰ Finally, the solution was quenched into an ice-water bath and washed by acetone and ethyl alcohol to remove the PVP and EG and centrifuged at 9000 rpm for 20min. The final AgNWs were dispersed into ethyl for further use.

Preparation of the AgNWs/PEDOT:PSS composites

55 The PEDOT:PSS solution was obtained from Sigma Aldrich

(OrgaconTM N-1005), and came into use without any further treatment.

Firstly, the as-prepared Ag nanowires dispersion solution was added into the PEDOT:PSS solution with different mass fractions 60 (0wt%, 5wt%, 10wt%, 15wt%, 20wt%, 25wt%, 30wt%) and mixed it by ultrasound and magnetic stirringfor 6 hours. Secondly, the mixed solution was poured to pre-cleaned glass gardens and then dried into the film at 300K. Then the film was washed by deionized water and ethanol for several times and 65 dried at 360K. After that, the composites film was scratched and grinded into the powders by a cryogenic grinding machine (SPEXSamplePrep 6770 Freezer/Mill, TECH-Knowledge International Co., California, U.S.A.).Samples containing different AgNWs mass fractions (0wt%,5wt%, 10wt%, 15wt%, 70 20wt%, 25wt%, 30wt%), plugs and impactor were embedded in a grinding vial, and the vial was precooled in the liquid nitrogen to make the samples brittle. The samples were ground into powders -195.6°C for 20min. Finally, the as-milled at AgNWs/PEDOT:PSScomposites powders (0.3g for each AgNWs 75 concentration samples) were consolidated by spark plasma sintering (Dr. Sinter 725, Japan). The powders of all samples were loaded into cylindrical carbon dies with an inner diameter of 10 mm, and consolidated into the pellets at 100°Cfor a dwell time of 5 minunder 50MPa, the final samples were the cylinders with the so mean size of diameter \times thickness = 10mm \times 2.0 mm.

Characterization

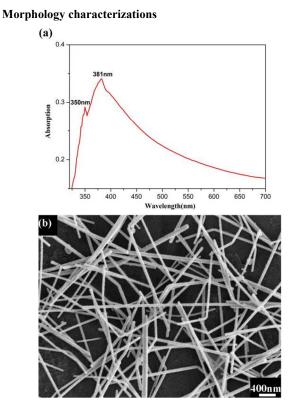
The UV-visible absorption spectra were measured on LanbdaA35 spectrometer (USA) at room temperature. The purity of the each phase in the AgNWs/PEDOT:PSS composites was characterized ⁸⁵ by X-ray powder diffraction (XRD, Rigaku D/Max-82550PC, Japan) with Cu K α radiation at 40kV, 200mA. The chemical structures of the as-prepared and SPSedPEDOT:PSS samples were investigated by Nicolet 8700 FTIR spectrometer. The spectra of FTIRwas collected by the averaging of 32 scans ranging from 500 to 4000 cm⁻¹. The field-emission scanning electron microscopy (FE-SEM, S-4800) was employed to study and observed the surface morphology of the bulk sample and the morphology of the pure AgNWs.

As for thethermoelectric properties, all samples were measured in ⁹⁵ the temperature range of 300K-360K.The thermal conductivity (κ) of the bulk sample was calculated through combining thermal diffusivity (a), heat capacity (Cp) with density (ρ) of the sample, according to the calculation:

$\kappa = a \times C_p \times \rho(2)$

¹⁰⁰ The thermal diffusivity was measured by a laser-flash system (LFA427; Netzsch Instruments, Selb, Germany), the samples are the cylinders with the mean size of diameter × thickness = 10mm × 1.8mm. The heat capacities were measured by Differential Scanning Calorimetry (Netzsch DSC 204 F1). The electrical ¹⁰⁵ resistance and Seebeck coefficient were characterized by Seebeck Coefficient/Electric Conductivity Measuring System (ZEM-3), the samples are the rectangles with the mean size of length × thickness × width = 8.5mm × 1.6mm × 3.3mm. Then the Hall coefficient R_H was carried out on a Hall measurement system ¹¹⁰ (Lakeshore HMS-7700, USA) with a magnetic field of 5G and an electrical current of 3mA.

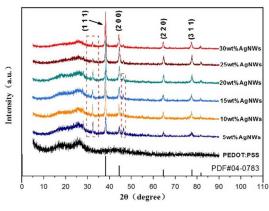
Results and discussion



5 Fig.1. (a) UV-visible absorption spectrum of as-prepared AgNWs. (b) FE-SEM image of as-prepared AgNWs.

The as-prepared AgNWs are studied by UV-visspectroscopy, as is shown in Fig.1a. The two peaks appearing at 350nm and 381nm corresponds to the surface plasmon resonance (SPR) of the

 10 AgNWs. 30 Through the FE-SEM image (Fig.1b), it can be seen that the as-prepared AgNWspossesshigh quality and quantity. These nanowires have the average length of 2-4 μ m and diameter of 60 nm.



15 Fig.2. X- ray diffraction of AgNWs/PEDOT:PSSbulk samples with different contents of AgNWs

Fig.2 shows the X-ray diffraction patterns of the AgNWs/PEDOT:PSScomposites. The broad peak at 25° indicates the phase of PEDOT:PSS.³¹The sharp peaks at 2θ values of 20 38.179°, 44.340°, 64.50°, 77.40°, 81.561° corresponding to (11

1), (2 0 0), (2 2 0) and (3 1 1), respectively, can be attributed to the pure phase of Ag (JCPDS File No. 04-0783),indicating the existence of Ag phase in the composites.^{23, 32}The small peaks at 20 values of 32° and 46° (markedbythe red dashed square)can be ²⁵ attributed to the oxidized composites of Ag and Na, which probably formed during the preparation of AgNWs.²⁵

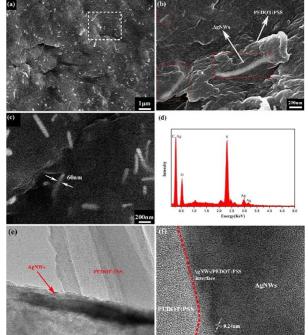


Fig.3. (a)FE-SEM (BSE model) image of AgNWs / PEDOT:PSSbulk sample with 20wt%AgNWs.(b) The interface (SE model)between the AgNWs and PEDOT:PSS matrix. (c) Higher magnification of white squared area of image (a). (d) EDX pattern of the composites.(e), (f) HR-TEM images of the samples with 20wt% AgNWs content.

The FE-SEM micrographs of the AgNWs/PEDOT:PSS composites containing 20wt% AgNWs are presented in Fig.3. It is obvious that the AgNWs are well-dispersed in the PEDOT:PSS matrix according to the Fig.3a. The red squared areas in Fig.3b show the interface and junction between the embedded AgNWs and polymer matrix, confirmingthat the close connection between the AgNWs and molecule chains of PEDOT:PSS.In Fig.3c, 40 clearly that the diameter of dispersed AgNWs is about 60nm, matchingthat of as-prepared AgNWs in Fig.1b. Fig.3d is the EDX pattern of the composites sample, showing the presence of major elements C, O, S and Ag, corresponding to the PEDOT:PSS

matrix and AgNWs.This confirms that AgNWs survive in the ⁴⁵ matrix during the consolidation process. Fig.3e clearly shows the a single AgNW is embedded in the PEDOT:PSS matrix (by HR-TEM image). Andin its higher magnification HR-TEM image, as shown in Fig.3f, the interplanardistance of 0.24nm agrees with that of the(1 1 1) lattice

⁵⁰ planes of Ag, clearly proving the organic-inorganic interface between PEDOT:PSS matrix and AgNWs. Therefore, the results of XRD, FE-SEM and HR-TEM fully demonstrate the existence of AgNWs and their homogeneous dispersion in the PEDOT:PSS matrix, as well as the organic-inorganic interface between ⁵⁵ PEDOT:PSS and AgNWs. 65

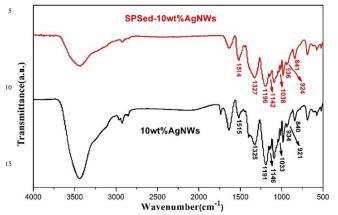
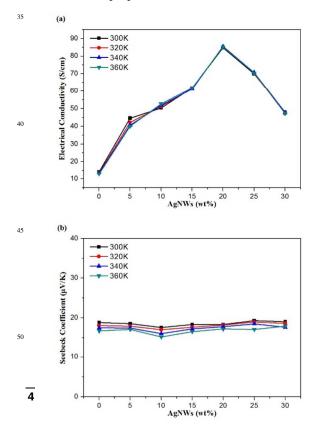


Fig.4. FTIR spectra of the AgNWs/PEDOT:PSSwith 10wt% AgNWs ²⁰ To investigate whether there exists any chemical changes during the consolidation process, we studied the FTIR spectra of the composite powders with 10wt% AgNWsand its SPSed bulk sample. As shown in Fig.4, the peak at 1325cm⁻¹ and 1518cm⁻¹ can be ascribed to the C-C and C=C stretching in the thiophene ²⁵ ring.Peak at 840cm⁻¹ is corresponding to the vibration mode of C-

S bonds in the thiophene ring.³³ The peaks at 1146cm⁻¹ and 1033 cm⁻¹ are assigned to the stretchingmodes of ethylenedioxy group, and the peak at 921cm⁻¹ can be attributed to the ethylenedioxy ringdeformation mode. The peak at 937cm⁻¹ and 1188cm⁻¹ are ³⁰ corresponding to –SO and S-OH stretching in the molecule of the PSS.³⁴From Fig.4, there did not show any obvious changes compared to the as-prepared powders, implying no chemical changes happened during the SPS press process.

Thermoelectric properties



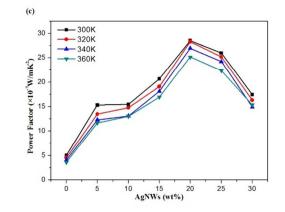


Fig.5. (a) Electrical conductivity (b) Seebeck coefficient (c) Power factor of the composites with different AgNWs contents at different temperatures

		1		
Samples	Volume	Carrier	Carrier	Seebeck
PEDOT:PSS +	density	concentration	mobility	coefficient
x wt%AgNWs	(g/cm^3)	(10^{19}cm^{-3})	$(cm^2V^{-1}s^{-1})$	$(\mu V/K)$
x=0	0.929	10.25	0.85	18.8
x=5	1.205	10.34	2.73	18.5
x=10	1.225	14.02	2.24	17.6
x=15	1.280	11.01	3.48	18.4
x=20	1.375	11.50	4.57	18.3
x=25	1.393	9.85	4.43	19.3
x=30	1.552	9.94	3.01	19.0

Table.1. Volume density, Carrier concentration, Carrier mobility and Seebeck coefficient of all bulk samples at room temperature.

- Measurements have beencarried out to study the effect of different AgNWs contents (0wt%, 5wt%, 10wt%, 15wt%, 20wt%, 25wt%, 30wt%) on the thermoelectric properties of PEDOT:PSS bulk samples. All samples were measured in the rs temperatures ranging from 300K to 360K. As can be seen in Fig.5a, the electrical conductivity firstly increases as the AgNWs content increases. Then it reaches the maximum value of 84.84 Scm⁻¹ for the composite with the AgNWs content of 20wt%, finally slightly decreases with the continuous increase in the so AgNWs content. It does not change too much with the increasing
- temperature, exhibiting the typical conducting polymer behavior.^{5, 23, 35, 36}As is known, electrical conductivity is calculated by the Eq.3:

$\sigma = ne\mu(3)$

- ⁸⁵ Where n is carrier concentration, e is electron charge and μ refers to the carrier mobility. So thechangesin electrical conductivity must be attributed to the changes in carrier concentration or carrier mobility caused by the introduction of AgNWs.The maximum value (84.84 Scm⁻¹) is six times as large as that of the
 ⁹⁰ pure PEDOT:PSS (14.23Scm⁻¹) at room temperature. It is also much higher than that of TeNWs/PEDOT:PSS pellets (about 55 Scm⁻¹) and Ag-PEDOT (6.49 Scm⁻¹) bulk pellet reported before.^{37, 7, 21} This high electrical conductivity value may be
 ⁹⁵ attributed to the interfacial interaction between the polymer matrix and AgNWs, leading to higher degree of organization of polymer molecules.^{3,38,36}
 - In the conventional inorganic TE materials, it has been

demonstrated that the Seebeck coefficient of the composites should follow the Eq.4:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T\left(\frac{\pi}{3n}\right)^{\frac{2}{3}} (4)$$

Where k_B, h, m*, and n are Boltzmann constant, Planck constant, ⁵ effective mass of carrier, and carrier concentration respectively.²⁶ Generally, the relationship between electrical conductivity and Seebeck coefficient is always inverse because Seebeck coefficient decreases with increasing carrier concentration. But here, Fig.5b

- shows that Seebeck coefficient almost keeps constant (19-10 16µV/K) after the introduction of AgNWs,in spite of the large increase in electrical conductivity. Thissuggests that the carrier
- follow a totally different electrical transport mechanism from that of the conventional materials.
- ¹⁵ To clarify the electrical transport properties in the composites, we measured carrier concentration at room temperature by Hall measurement system. According to the Table.1, there is no obvious change in the carrier concentration with increasing AgNWs contents. Consequently, the carrier mobility is enhanced
- ²⁰ by almost fivetimes with 20wt% AgNWsaddition.As is reported, the PEDOT:PSS is sensitive to the polymer morphology, and a highly-ordered structure is conducive to obtaining a high electrical conductivity.^{39, 40} When AgNWs are embedded into the PEDOT:PSS matrix, it may create a kind of organic-inorganic
- ²⁵ interfaces (shown in Fig.3b). This kind of interfaces will not only assist the PEDOT:PSSchains to exhibit a higher level of ordered structure than bulk PEDOT:PSS, but also provide more conductive paths between the PEDOT:PSS chains to facilitate the carrier transport as conducting bridges.^{3, 15, 41} Furthermore, the
- ³⁰ introduction of AgNWs may also reduce the carrier-hopping barriers, thus creating a much higher carrier mobility.^{22, 42} When the content of AgNWs reaches 25wt% and 30wt%, the carrier mobility slightly decreases. This suggests that embedded AgNWs will not always increase the conducting paths, too many AgNWs
- ³⁵ may even impede the carrier transport. The carrier concentration of the composites is relatively unchanged, and that is why the Seebeck coefficient can keep its value with the increasing electrical conductivity. The embedded AgNWs may lead to the carrier filter effect, which is believed to hinder the transport
- ⁴⁰ oflow-energy electrons acrossthe organic-inorganic interfaces, and leaving the Seebeck coefficient insensitive tothe changes in electrical conductivity and effectively decouplingthese two properties.^{24, 43, 44}This indicates the reason why embedded AgNWs can improve the carrier mobility of the bulk composites
- ⁴⁵ while not change the level of the carrier concentration. Combining the values of Seebeck coefficient and electrical conductivity, the power factor increases from 5.03×10⁻⁷WmK⁻² to 28.55×10⁻⁷WmK⁻² at room temperature, achieving a five-time enhancement (as shown in Fig.5c). Actually, some works even
- ⁵⁰ achieved the simultaneous enhancement in electrical conductivity and Seebeck coefficient before, such as the TeNWs/PEDOT:PSS thin film reported by Coates.³And similar enhancements happen in the PANI system.^{15, 38}All these works and results suggest that the low dimensional nano-sized materials cansignificantly
- ⁵⁵ optimize electrical transport properties of the conducting polymers matrix and lead to a new model to improve the power factor of organic TE materials.

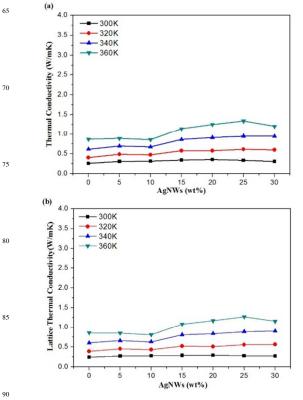


Fig.6. (a) Thermal conductivity of the composites with different AgNWs contents at different temperatures. (b) Lattice thermal conductivity of the composites with different AgNWs contents.

composites with different Agiv ws contents.		
Samples PEDOT:PSS + x wt% AgNWs	Thermal diffusivity (mm ² /s)	
x=0	0.220	
x=5	0.201	
x=10	0.181	
x=15	0.159	
x=20	0.178	
x=25	0.169	
x=30	0.143	

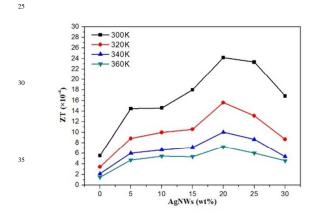
Table.2. Thermal diffusivity of allsamples at room temperature

⁹⁵ Fig.6a shows temperature-dependent thermal conductivity with different AgNWs contents. The thermal conductivity increases with increasing temperatures because of the increasing Cp of the samples. Interestingly, we find κ does not raise too much with increasing AgNWs contents. It changes from 0.257W/mK to 0.356W/mK, and the average value of thermal conductivity still remains at low level of 0.3W/mK at room temperature, which is very close to that of pure PEDOT:PSS.²² Generally, the thermal conductivity of the materials is determined by two parts: electronic thermal conductivity (κ_e) and lattice thermal los conductivity (κ_L). According to the Wiedemann–Franz law:

$\kappa_e = L\sigma T(5)$

Where L is the Lorenz constant, σ is the electrical conductivity and T is the temperature. Therefore, κ_L is usually obtained by directly subtracting the κ_e from κ .^{22, 45} It need to be noted thatin conducting polymers, the correlation between κ and σ is weak, indicating the changes in κ of the composites mainly depends on κ_L .^{9, 45} To our knowledge, Ag possesses a large intrinsic thermal conductivity (about 400W/mK), which would make huge ⁵ enhancement in κ_L .⁴⁶However, as shown in Fig.6b, the lattice

- thermal conductivity of the composites is about 0.27 W/mK at room temperature, does not increase obviously (L is taken to 2.45 $\times 10^{-8}$ V²K⁻²)^{22, 47}. This thermal behavior can be attributed to the nano-interfaces between the embedded AgNWs and polymer wattrive, which enhances the castering of the long wavelength.
- ¹⁰ matrix, which enhances the scattering of the long-wavelength phonons and impedes the phonon transport across this interface.^{43, 45} Table.2 shows the thermal diffusivity of all samples at room temperature.It is clear that with increasing AgNWs, the thermal diffusivity decreases from 0.220 for pure PEDOT:PSS to
- ¹⁵ 0.143. This decrease may be in good agreement with the tougher phonon transport caused by the different AgNWs contents in the composites.^{21, 45} The phonon scatter eliminates most of the possible huge increase in κ_L as well as increasing κ_e . Therefore, it finally keeps a relatively constant value of κ . On another point of
- $_{20}$ view, the decrease in thermal diffusivity can eliminate the increase in density of the composites (shown in table.1). According to the Eq.2, because of the relatively constant C_p , the calculated value of the κ almost remains the same at room temperature.



⁴⁰ Fig.7. ZT merit of the samples with different AgNWs contents at different temperatures.

The ZT of the samples are calculated and shown in Fig.7.the highest value is 2.42×10^{-3} for the composites with 20wt% AgNWs at 300K, achieving more than four-times enhancement ⁴⁵ compared to the pure bulk PEDOT:PSS (ZT= 5.5×10^{-4}). Although

theZT value of the composites isnot impressive compared to that of PEDOT:PSS-based hybrid thin films, the electrical conductivity is relatively high among the bulk PEDOT:PSS TE materials.^{10, 22, 24, 48}More important is that this enhancement in ZT

- ⁵⁰ is gained by raising the electrical conductivity without sacrificing the value of Seebeck coefficient or raising the thermal conductivity, and seems to be an ideal mode for us to fabricate high-performance bulk PEDOT:PSS TE materials. If we can realize an ordered structure in a bulk PEDOT:PSS system through
- ⁵⁵ some post or pro treatment process, we may achieve a much higher ZT value and closer the gap from that of thin films.⁸Our further works will focus on how to realize the simultaneous enhancement in electrical conductivity and Seebeck coefficient

for the bulk PEDOT:PSS.

60 Conclusion

In summary, we successfully prepared higher-performance AgNWs/PEDOT:PSS bulk TE materials by the as-prepared composites powders. The resultsshow that the introduction of AgNWsmay lead to the potential organic-inorganic interfaces, ⁶⁵ which can significantly enhances the carrier mobility and electrical conductivity. Furthermore, the introduction of AgNWswill not sacrifice the Seebeck coefficient and increase the thermal conductivity too much. We find sample with 20wt% AgNWs has the highest electrical conductivity (84.84Scm⁻¹), ⁷⁰ making a five-times enhancement compared to the pure PEDOT:PSS, and the highest ZT value is achieved as 2.42×10⁻³ at room temperature. All these results demonstrate that the addition of low dimensional AgNWsand even other low dimensional materials may be the promising choice to improve ⁷⁵ the performance of bulk organic TE materials.

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Notes and references

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- 1.H. K. Lyeo, A. A. Khajetoorians, L. Shi, K. P. Pipe, R. J. Ram, A. Shakouri and C. K. Shih, *Science*, 2004, **303**, 816.
- 2.M. He, F. Qiu and Z. Lin, Energ. Environ. Sci., 2013, 6, 1352.
- K. Coates, S. K. Yee, B. McCulloch, K. C. See, A. Majumdar, R. A. Segalman and J. J. Urban, Adv. Mater., 2013, 25, 1629.
- 4.O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren and X. Crispin, *Nat. Mater.*, 2011, **10**, 429.
 - 5.Q. Zhang, W. Wang, J. Li, J. Zhu, L. Wang, M. Zhu and W. Jiang, J. Mater. Chem. A, 2013, 1, 12109.
 - 6.Y. Hu, S. Norina and T. Naoki, *J. Therm. Anal. Calorim.*, 2002, **69**, 881. 7.F. X. Jiang, J. K. Xu, B. Y. Lu, Y. Xie, R. J. Huang and L. F. Li, *Chinese*
 - *Phys. Lett.*, 2009, **25**, 2202.
 - 8.C. Liu, F. Jiang, M. Huang, R. Yue, B. Lu, J. Xu and G. Liu, *J. Electron. Mater.*, 2011, **40**, 648.
 - 9.G. H. Kim, L. Shao, K. Zhang and K. P. Pipe, Nat. Mater., 2013, 12, 719.
- 105 10.Y. Du, K. F. Cai, S. Chen, P. Cizek and T. Lin, ACS appl. mater. inter., 2014, 6, 5735.
 - 11.R. Venkatasubramanian, E. Siivola, T. Colpitts and B. O'Quinn, *Nature*, 2001, **413**, 597.
 - 12.L. M. Goncalves, P. Alpuim, A. G. Rolo and J. H. Correia, *Thin Solid Films*, 2011, **519**, 4152.
 - 13.T. C. Harman, M. P. Walsh, B. E. Laforgeand G. W. Turner, J. Electron. Mater., 2005, 34, 19.
 - 14.D. Yoo, W. Son, S. Kim, J. J. Lee, S. H. Lee, H. H. Choi and J. H. Kim, *RSC Adv.*, 2014, **4**, 58924.
- 115 15.Q. Yao, Q. Wang, L. Wang and L. Chen, *Energy Environ. Sci.*, 2014, 7, 3801.
 - 16.J. Ouyang, ACS appl. mater. inter., 2013, 5, 13082-13088.
 - 17.D. J. Yao, C.J. Kim and G. Chen, 20th International Conference on

Thermoelectrics, Beijing, 2001.

- 18.R. Yang, J. Appl. Phys., 2004, 95, 8226.
- 19.G. S. Hwang, A. J. Gross, H. Kim, S. W. Lee, N. Ghafouri, B. L. Huang, C. Lawrence, C. Uher, K. Najafi and M. Kaviany, *Int. J. Heat Mass Trans.*, 2009, **52**, 1843.
- 20.K. H. Lee and O. J. Kim, Int. J. Heat Mass Trans., 2007, 50, 1982.
- 21.Y. Wang, K. Cai, S. Chen, S. Shen and X. Yao, J. Nanopart. Res., 2014. 16, 2531.
- 22.G. H. Kim, D. H. Hwang and S. I. Woo, *Phys. Chem. Chem. Phys.*, 2012, 14, 3530.
- 23.W. Wang, S. Sun, S. Gu, H. Shen, Q. Zhang, J. Zhu, L. Wang and W. Jiang, *RSC Advances*, 2014, **4**, 26810.
- 24.G. P. Moriarty, S. De, P. J. King, U. Khan, M. Via, J. A. King, J. N. Coleman and J. C. Grunlan, J. Polym. Sci. Pol. Phys., 2013, 51, 119.
- 15 25.Q. Zhang, X. Ai, W. Wang, L. Wang and W. Jiang, Acta Mater., 2014, 73, 37.
 - 26.Q. Zhang, X. Ai, L. Wang, Y. Chang, W. Luo, W. Jiang and L. Chen, *Adv. Funct. Mater.*, 2014, DOI: 10.1002/adfm.201402663.
 - 27.L. Hicks and M. Dresselhaus, Phys. Review B, 1993, 47, 16631.
- 20 28.A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J. K. Yu, W. A. Goddard, 3rd and J. R. Heath, *Nature*, 2008, 451, 168.
- 29.M. S. Dresselhaus, G. Chen, M. Y. Tang, R. G. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J. P. Fleurial and P. Gogna, *Adv. Mater.*, 2007, **19**, 1043.
- 25 30.Y. Sun, Y. Yin, B. T. Mayers, T. Herricks and Y. N. Xia, *Chem. Mater.*, 2002,14,4736.
 - 31.H. Song, C. Liu, H. Zhu, F. Kong, B. Lu, J. Xu, J. Wang and F. Zhao, J. Electron. Mater., 2013, 42, 1268.
- 32.N. Duraisamy, S.-J. Hong and K.-H. Choi, *Chem. Eng. J.*, 2013, **225**, 887.
 - 33.D. Han, G. Yang, J. Song, L. Niu and A. Ivaska, J. Electroanal. Chem., 2007, 602, 24.
 - 34.B. D. Martin, N. Nikolov, S. K. Pollack, A. Saprigin, R. Shashidhar, F. Zhang and P. A. Heiney, *Synthetic Met.*, 2004, **142**, 187.
- ³⁵ 35.W. Wang, Q. Zhang, J. Li, X. Liu, L. Wang, J. Zhu, W. Luo and W. Jiang, *RSC Adv.*, 2014, 5, 8988.
 - 36.S. K. Yee, N. E. Coates, A. Majumdar, J. J. Urban and R. A. Segalman, *Phys. Chem. Chem. Phys.*, 2013, 15, 4024.
- 37.K. C. See, J. P. Feser, C. E. Chen, A. Majumdar, J. J. Urban and R. A. Segalman, *Nano letters*, 2010, **10**, 4664.
- 38.Q. Yao, Q. Wang, L. Wang, Y. Wang, J. Sun, H. Zeng, Z. Jin, X. Huang and L. Chen, J. Mater. Chem. A, 2014, 2, 2634.
- 39.P. K. Choudhury, D. Bagchi, C. S. S. Sangeeth and R. Menon, J. Mater. Chem., 2011, 21, 1607.
- 45 40.E. Çinar, S. Koçyiğit, A. Aytimur, I. Uslu and A. Akdemir, *Metal. Mater. Trans. A*, 2014, 45, 3929.
- 41.N. G. Semaltianos, S. Logothetidis, N. Hastas, W. Perrie, S. Romani, R. J. Potter, G. Dearden, K. G. Watkins, P. French and M. Sharp, *Chem. Phys. Lett.*, 2010, **484**, 283.
- 50 42.Q. Yao, L. Chen, X. Xu and C. Wang, Chem. Lett., 2005, 34, 522.
- 43. D. Kim, Y. Kim, K. Choi, J. C. Grunlan and C. H. Yu, ACS Nano, 2010, 4, 513.
- 44.Y. S. Kim, D. Kim, Kaylan J. Martin, C. Yu, J. C. Grunlan, *Macromol. Mater. Eng.*, 2010, **295**, 431.
- 55 45.Q. Jiang, C. Liu, J. Xu, B. Lu, H. Song, H. Shi, Y. Yao and L. Zhang, J. Polym. Sci. Pol. Phys., 2014, 52, 737.
 - 46.A. J. Minnich, M. S. Dresselhaus, Z. F. Ren and G. Chen, *Energy Environ. Sci.*, 2009, 2, 466.
 - 47.H. L. Kwok, J. Mater. Sci.-Mater. EL., 2014, 26, 830.
- 60 48.A. Yoshida and N. Toshima, J. Electron. Mater., 2013, 43, 1492.