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N-type CNTs/Ag₂Te Nanohybrid Buckypaper with High Thermoelectric Figure-of-merit

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ABSTRACT

N-type thermoelectric materials was made from CNT buckypapers. We used Ag₂Te to achieve electron injection to the CNTs. The thermoelectric characterizations on more than 50 samples show that the CNTs/Ag₂Te hybrids exhibit negative Seebeck coefficients (e.g. n-type) of -30 to -228 $\mu\text{V/K}$. Meanwhile, the tunneling coupling between the CNTs and Ag₂Te increase the electrical conductance to the range of 10000 ~ 20000 S/m, which is higher than each single component (CNTs or Ag₂Te). These n-type TE buckypapers are flexible and robust with ZT values 1~2 orders of magnitude higher than previously reported for CNTs based TE materials. In addition, the preparation of such buckypapers are very simple as compared to traditional inorganic process without need for hot pressing or spark sintering. These n-type TE buckypapers can provide important

components for fabricating CNT based flexible TE devices with good conversion efficiency.

KEYWORDS

Carbon nanotube, Silver telluride, Thermoelectric, Figure of merit, Seebeck, Flexible

INTRODUCTION

In the past decades, thermoelectric (TE) materials have achieved great enhancements in converting waste heat to power.^{1, 2} The efficiency of TE materials, figure of merit ZT can be expressed as $ZT = S^2\sigma T/\kappa$, where S is Seebeck coefficient, σ is electrical conductivity, T is absolute temperature and κ is thermal conductivity. To obtain advanced efficiency of TE materials, high Seebeck coefficient, high electrical conductivity and low thermal conductivity are required. Many efforts on enhancing TE performances in recent years are nanostructuring the materials and hence significantly decrease the thermal conductivity.³⁻⁶ So far, most of the advanced TE materials are reported on inorganic crystals,⁷⁻¹³ which are rigid and brittle. In many times, the TE devices made from these inorganic crystals may be subjected to failure under continuous thermal cycling due to the mismatch of the thermal expansion among different components. Some strategies have been developed to solve this issue. For example, it has been reported that carbon nanotubes can be used as the interface material to combine with Bi_2Te_3 to improve the thermomechanical compliance.¹⁴ Development of flexible thermoelectric materials is another attractive approach. Organic materials such as conducting polymers were reported as flexible thermoelectric materials.¹⁵ But those materials often have low electrical conductivity ($< 500 \text{ S/m}$), which leads to low ZT value.^{16, 17} And also it may be difficult to expand their application into high temperature range, e.g. $>500 \text{ K}$.¹⁸

Carbon nanotube (CNT) has many advantages such as chemically stable^{19, 20}, highly electrically conductive^{21, 22} and mechanically robust^{23, 24}. Owing to these advanced properties as well as abundance of carbon on the earth, CNT is an important candidate to build flexible electronics.²⁵⁻²⁷ However, it is seldom regarded as a TE material due to its

poor Seebeck coefficient ($< 60 \mu\text{V/K}$)²⁸ and high thermal conductivity of a single tube ($\sim 250\text{-}10000 \text{ Wm}^{-1}\text{K}^{-1}$ for single tube or aligned arrays)²⁹⁻³¹. It has been reported that low thermal conductivities can be obtained in CNTs/conductive polymer composites and processed tubes.³² For example, combining CNTs with polyaniline can reduce thermal conductivity to $\sim 0.5 \text{ Wm}^{-1}\text{K}^{-1}$.³³ Also in our previous reported work, plasma treated CNT buckypaper show attractive p-type Seebeck values of $\sim 350 \mu\text{V/K}$ while the electrical conductivity still maintain an acceptable value ($\sim 1000 \text{ S/m}$).³⁴ Hence, CNT based materials still hold the promising potential to achieve TE properties comparable to some of the reported traditional inorganic materials, such as BiSbTe^{35,36} or PbTe³⁷⁻³⁹. Based on reported literatures, more studies on p-type behavior were reported for TE measurement of CNT related samples.⁴⁰⁻⁴³ So far, although there are a few works on n-type CNT related materials, either low Seebeck value^{44, 45} or low electrical conductivity⁴⁶ are obtained and only low ZT values $\sim 10^{-3}$ are achieved⁴⁷. Hence, more efforts should be done to achieve ZT to an acceptable value (e.g. > 0.1) which is comparable to traditional inorganic materials. Development of such n-type TE materials is encouraging to provide important components for fabricating CNT based flexible TE devices.

Herein, we report the preparation of n-type TE materials of Ag₂Te decorated single-walled CNTs (Sigma-Aldrich, carbon $>90\%$, $\geq 77\%$ carbon as SWCNT) (CNTs/Ag₂Te). The sample was prepared via an oil phase step and then processed into flexible buckypapers. The size of the Ag₂Te particle is around 10 nm. The mass ratio between CNTs and Ag₂Te can be easily tuned by varying the precursor ratio. The thermoelectric characterizations on more than 50 samples show that the CNTs/Ag₂Te hybrids exhibit negative Seebeck coefficients (e.g. n-type) of -30 to $-228 \mu\text{V/K}$. The electrical

conductivity increases for samples with higher amounts of Ag₂Te and can reach the range of 10000 to 20000 S/m. The measured thermal conductivity for such hybrid buckypapers can be as low as $\sim 0.7 \text{ Wm}^{-1}\text{K}^{-1}$ in the temperature range of 325~525 K. If we do not consider the anisotropic aspect of such buckypaper (e.g. this assumption allows us to calculate the figure of merit, ZT , based on the measured electric conductivities, Seebeck coefficients and thermal conductivities), the estimated highest figure of merit ZT of CNTs/Ag₂Te hybrids was 0.44 ($\pm 5\%$) at 525 K. Such ZT value is comparable to some of the traditional thermoelectric materials and is higher than that of either pristine CNT or pure Ag₂Te.

EXPERIMENTAL SECTION

Synthesis. In a typical synthesis, silver precursor was first prepared by 170 mg (1 mmol) AgNO₃ dissolving in 10 ml D.I. water in a flask. Then 10 ml toluene with 0.24 ml (1 mmol) 1-Dodecanethiol were added into the solution and well stirred for 1 h at room temperature for ligand attachment. After that, the stirring was stopped and the solution was self divided into two phase. Next, the clear aqua phase at the bottom of the flask was removed. The CNTs (1 mg, 3 mg and 5 mg) were dispersed in toluene via 2 h ultrasonication. Then the well dispersed CNTs were added into the silver precursor solution first. The temperature was increased to 383 K and maintains 10 min or so. After then, 0.5 ml TOP-Te solution (1M) was injected into the as-prepared solution and stir for 2 min at 383 K. The 1M TOP-Te solution was prepared via dissolving 1.276 g Te powder into 10 ml trioctylphosphine. After 2 min reaction, the flask was quickly quenched in cold water. Next, the sample solution was further dissolved in hexane and then washed by

ethanol for 2-3 times. The washed solutions were dropped cast onto copper foils and dried in the oven with the temperature of 333 K. After the solvent evaporated, the Ag₂Te/CNT sheets were self peeled off from the copper foils. To remove the *-thiol* capping on the samples, the samples were annealed in Ar at 673 K for 1 hour. For Ag₂Te sample, since it was not flexible enough to make a free standing sheet, the powder was collected and hot pressed into pellet in Ar at 673 K.

Characterization techniques. The morphology and nanostructures of the samples were characterized using XRD (Bruker D8 Powder), FESEM (JEOL JSM7600) and TEM (JEOL JEM-2100F). The TEM samples were prepared by dropping the solutions onto copper grids and annealed the whole copper grid in Ar at 673 K. Hall measurement was carried out using Hall system HL 5500 at room temperature under the Van Der Pauw mode. The Seebeck coefficient and resistivity were measured from 323 K to 523 K using the ZEM-3 Seebeck meter under helium environment (Figure S1). The samples were cut into a rectangular piece with dimension of 10 × 4mm² and fixed on a glass substrate by applying silver paste to both ends. The samples for thermal conductivity measurements were cut into 12.7 × 12.7 mm² (CNTs/Ag₂Te hybrid and pure CNT buckypaper) or polished into the round pellet with the diameter of 12.7 mm (Ag₂Te pellet) and were measured by laser flash (NETZSCH MicroFlash LFA457).

RESULTS AND DISCUSSIONS

Five types of samples including pure Ag₂Te, pure CNTs and three CNTs/Ag₂Te hybrids were prepared for characterization and TE properties measurements. The CNTs/Ag₂Te hybrid samples were prepared by injecting TOP-Te into oil phase solution contained Ag

precursor, CNT and surfactant 1-dodecanethiol. The weight ratios of CNT Ag₂Te can be adjusted by changing the amount of CNT and estimated based on the amount of precursor added. The estimated weight ratios of CNT to Ag₂Te of three hybrid composites were: 1:17, 3:17 and 5:17, and named as CA-1, CA-2 and CA-3, respectively. Figure 1A is the optical image of the buckypaper of sample CA-1. It was prepared via dropping casting the washed CNTs/Ag₂Te hybrid solution onto copper foil and peeling off the free standing paper after drying. The buckypapers were then annealed at 673 K. The obtained buckypaper was around 50 μm in thickness and mechanically robust upon repeated bending. The low magnification field emission scanning electron microscopy (FESEM) image of hybrid sample CA-1 (Figure 1B) indicates that the CNT bundles were entangled randomly. Figures 1C-E are transmission electron microscopy (TEM) images that show the morphology and structure of the hybrid sample CA-1. It can be found that most Ag₂Te particles attached on the CNT walls are around 10 nm. Small particles may agglomerate and form large particles during the annealing process. One large particle of around 25 nm, which is denoted by the arrow, can also be observed (Figure 1C). Additionally, we can find that the diameter of a single CNT is < 1 nm, but the CNTs may self-assemble into bundles (Figure 1D) due to the van der Waals force. The diameters of CNT bundles shown in Figures 1C and D are around 10 nm. Figure 1E is a high resolution TEM (HRTEM) image of an Ag₂Te particle on CNT walls. It indicates that the Ag₂Te particle is single crystalline. The representative X-ray diffraction (XRD) pattern of CA-1 is shown in Figure 1F, which matches the monoclinic Ag₂Te phase (JCPDS 34-0142). There is no detectable impurity phase.

For comparison purpose, pure Ag_2Te and pure CNT samples were also prepared. Ag_2Te was synthesized by a similar method as that of CNTs/ Ag_2Te hybrids but without adding CNTs. Figure 2A shows the XRD pattern of pure Ag_2Te . Peaks corresponding to the monoclinic Ag_2Te phase (JCPDS 34-0142) can be observed. There is a reversible phase transition of Ag_2Te at 418 K from β phase with a monoclinic structure to α phase with a face centered cubic (fcc) structure. Although the samples were annealed at 673 K after synthesis, no impurity phase except for the monoclinic Ag_2Te phase is detectable according to the XRD result. Thus, we believe that the Ag_2Te can easily convert back from fcc phase to monoclinic phase when the temperature returns to lower temperatures (<418 K). Figure 2B shows the TEM image of pure Ag_2Te particles. The nanoparticles are uniform with size of ~ 5 nm. Figure 2C is the FESEM image of pure CNT buckypaper. It shows a random network of CNT bundles. The average diameter of CNT bundles are around 10 nm.

For TE properties measurements, CNTs/ Ag_2Te hybrid buckypapers with the thickness ~ 50 μm were cut into proper size for different measurements. Pure CNTs were also prepared into flexible buckypaper for TE measurements. Pure Ag_2Te was rigid and brittle, so it cannot be prepared into a free standing sheet. Hence, Ag_2Te pellet was prepared via hot press at 673 K.

Electrical conductivity values of three CNTs/ Ag_2Te hybrid buckypapers (CA-1, CA-2 and CA-3) are shown in Figure 3A. It shows that samples with higher Ag_2Te content exhibit higher electrical conductivities at the same temperature range. CA-1 shows the highest electrical conductivity of 23500 S/m at 381 K. The shape of the electrical conductivity curves are similar for these three samples within the measurement

temperature of 325~550 K. The electrical conductivity of CNTs/Ag₂Te hybrids drops suddenly at temperature close to the phase transition point of Ag₂Te (i.e. 418 K). Below the phase transition point, the electrical conductivity becomes higher at increased temperature, which shows a typical semiconducting behavior. At temperature range of $T > 418$ K, the electrical conductivity decreases with the increase of temperature, which becomes a metallic/heavily doped semiconducting behavior. Pure Ag₂Te pellet and pure CNTs buckypaper were also measured for comparison. The electrical conductivity curve of pure Ag₂Te pellet displays a similar trend as that of CNTs/Ag₂Te hybrids. It increases at increased temperature below the phase transition point, and decreases at increased temperature above the phase transition point. The electrical conductivity of CNTs buckypaper is 3500 S/m to 5000 S/m in the measured temperature range. It decreases at increased temperatures, which shows a metallic/heavily doped semiconducting behavior. The electrical conductivity of CA-1 is higher than both pure CNTs buckypaper and pure Ag₂Te pellet, which shows the synergism in the CNTs/Ag₂Te hybrid structure similar to previous reported effect for binary nanocrystal superlattices.⁴⁸ The higher electrical conductivity of CA-1 compared to pure CNTs buckypaper is possibly related to doping effect. And the electrical properties of all CNTs/Ag₂Te hybrid samples and pure Ag₂Te pellet can be further studied with Hall Measurements at room temperature (Table 1). The mobility, μ , can be calculated via $\sigma = n\mu e$, where σ is electrical conductivity, n is carrier concentration and e is elementary charge. For the three CNTs/Ag₂Te hybrids, the carrier concentration is higher for samples with more Ag₂Te. The sample CA-1, which contains most Ag₂Te, has the largest carrier concentration of $6.591 \times 10^{18} \text{ cm}^{-3}$ among the three CNTs/Ag₂Te hybrids. This observation indicates that, during the Ag₂Te decoration

process, electrons are injected from Ag₂Te to CNTs. With the increase of Ag₂Te content, more electrons exist in the system, hence the carrier concentration increases. The mobilities of CNTs/Ag₂Te hybrids show non-monotonic trend. This is because that in these hybrid samples, Ag₂Te plays multiple roles including network element, electron donor, impurity, and so on. Therefore, their impact on the electronic properties is complex. For example, as network elements they provide extra transport channels helping enhance electron mobility, while those decorated onto CNTs scatter electrons. Thus combination of these interactions between composites and carriers possibly gives rise to non-monotonic mobility trend.^{49, 50} Additionally, we found that the mobilities of CNTs/Ag₂Te hybrids (120-250 cm²V⁻¹s⁻¹) are higher than pure Ag₂Te (12.702 cm²V⁻¹s⁻¹) by one order of magnitude. Although the electron scattering caused by the CNTs/Ag₂Te interfaces may be stronger than the Ag₂Te/Ag₂Te interfaces, the change of electron mean free path (MFP) should also be considered. Since Ag₂Te is nanoparticle, the electron MFP in Ag₂Te is shorter than the size of particle (i.e. 10 nm) and electron transport is limited by the size of nanoparticle. However, MFP can be much longer in CNTs, considering the length of CNTs (hundreds of nanometers to several micrometers) and their exotic transport property along the tube. Thus in hybrid samples, the average MFP is enhanced with CNTs as part of the network and mobilities are larger than that of pure Ag₂Te.

We mention that the effect of the irregularities in the nanoparticles positions and in the strengths of the tunneling coupling is different for metallic and insulating samples. If the coupling between the particles is sufficiently strong and the system is well conducting, the irregularities are not very important.⁵¹ In contrast, irregularities become crucial in the

limit of low coupling, where the system is an insulator. The key parameter that determines most of the physical properties of inhomogeneous samples is the dimensional tunneling conductance g between neighboring particles. Samples with $g > 1$ exhibit metallic transport properties, while those with $g < 1$ show insulating behavior. All our samples belong to the insulating side of the metal-insulator transition. Therefore, the charge on each particle becomes quantized as in the standard Coulomb blockade behavior. In this case, an electron has to overcome an electrostatic barrier of the order E_c in order to hop onto a neighboring particle, with E_c being the Coulomb energy of a single particle. At applied bias voltages and temperatures large enough to overcome local Coulomb energy costs, transport occurs by sequential tunneling between neighboring dots.⁵² At small bias and low temperatures, sequential tunneling is suppressed by the Coulomb blockade. In this regime, conduction involves higher order tunneling processes, the so-called cotunneling events, which can transport a charge over distances of several particles without incurring the full Coulomb energy costs. The above physics is valid for low temperatures, below 380K. At higher temperatures, above 380K our samples show metallic behavior meaning that the temperature reaches the size of the Coulomb gap. In this case, the number of electrons in the conducting band increases exponentially with temperature leading to metallic behavior: the higher the temperature the lower the conductivity. This behavior is the consequences of the fact that the number of phonons increases with temperature leading to more difficult electron propagation through the sample due to many scattering events.

Seebeck coefficients of three CNTs/Ag₂Te hybrid buckypapers samples display n-type properties (negative Seebeck coefficient) (Figure 3B). Generally, the absolute values of

Seebeck coefficients of three CNTs/Ag₂Te hybrids samples are larger at higher temperatures in the temperature range of ~418-550 K. Among them, CA-1 exhibits the highest Seebeck value of 228 $\mu\text{V/K}$ at 537 K. The two other hybrid samples, CA-2 and CA-3, also achieve Seebeck values of $>100 \mu\text{V/K}$ when the temperature is higher than 480 K. The maximum Seebeck value obtained for Ag₂Te pellet is 157 $\mu\text{V/K}$ at 421 K, which is ~100 K lower than that of CA-1. The CNTs buckypaper shows a lower p-type value (~30-50 $\mu\text{V/K}$) within the measured temperature range. The maximum Seebeck value of CA-1 is ~45% higher than that of pure Ag₂Te pellet and 4 times higher than that of pure CNTs buckypaper. The enhancement of Seebeck value for CA-1 may result from the change of density of states due to that the Ag₂Te dopants may generate some impurity levels in the band structures.

Combine with Seebeck coefficient and electrical conductivity, the power factors of the CNTs/ Ag₂Te hybrids, pure Ag₂Te and pure CNTs are calculated (Figure 3C). Due to the largest Seebeck values and highest electrical conductivity, sample CA-1 presents largest power factor than that of all the other samples. The highest power factor of CA-1 is 579 $\mu\text{W/mK}^2$ at 537 K, which is 2 times of pure Ag₂Te pellet's and 80 times of pure CNT buckypaper's values in the same temperature range.

Thermal Conductivities (Figure 3D) of selected samples, CA-1, pure Ag₂Te and pure CNTs were measured by laser flash. Sample CA-1 exhibits a low thermal conductivity of $\sim 0.7 \text{ Wm}^{-1}\text{K}^{-1}$, which is lower than that of pure Ag₂Te pellet and pure CNTs buckypaper in the same temperature range. Thermal conductivity, κ , can be expressed as $\kappa = \kappa_e + \kappa_L$, where κ_e and κ_L is electron thermal conductivity and lattice thermal conductivity, respectively. In the absence of inelastic processes, the electron thermal conductivity can

be estimated using Wiedemann-Franz relation $\kappa_e = L\sigma T$. Since Lorenz number cannot be accurately determined, the accurate value of κ_e can not be confirmed. But if we assume $L = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$, take the point of 525 K as an example, the electron thermal conductivity of CA-1, Ag_2Te and CNT can be estimated as 0.14, 0.1 and $0.05 \text{ Wm}^{-1}\text{K}^{-1}$, respectively. And the lattice thermal conductivity can be calculated then as 0.55, 0.68, $1.03 \text{ Wm}^{-1}\text{K}^{-1}$, respectively. Although sample CA-1 has the highest electron thermal conductivity due to the largest electrical conductivity, it exhibits the lowest lattice thermal conductivity mainly attributed to the strong phonon scattering of the hybrid structure. It is worth noting here that the Ag_2Te sample is a dense pellet prepared by hot press at 673 K while the CA-1 and pure CNTs sample are loosely packed buckypapers. The structural difference will also affect the lattice thermal conductivity. In general, the total thermal conductivity shows the non-monotonic temperature behavior due to competition between two different mechanisms. At high temperatures the number of phonons is large leading to larger thermal conductivity.

If we do not consider the anisotropic aspect of such buckypaper, the figure of merit, ZT , can be calculated, based on the measured electric conductivities, Seebeck coefficients and thermal conductivities. The estimated highest figure of merit ZT is 0.44 at 525 K on the sample CA-1. It is more than 2 times higher than that of pure Ag_2Te and 100 times higher than that of CNT. Although the thermoelectric performance of Ag_2Te based materials may be further enhanced with more efforts (e.g. tuning particle size⁵³), they are rigid and may have different working temperatures⁵⁴. Hence, CNTs/ Ag_2Te hybrid holds niche applications since it is flexible and robust.

CONCLUSION

In summary, we successfully synthesized n-type CNTs/Ag₂Te hybrids via solvothermal approach. The Ag₂Te particles attached on CNT bundles have small size of ~10 nm and these CNTs/Ag₂Te hybrids can be prepared into flexible buckypaper. The hybrid sample CA-1 shows higher electrical conductivity, higher Seebeck coefficient and lower thermal conductivity than that of pure Ag₂Te and pure CNTs in the temperature range of 325 K-525 K. These enhancements may attribute to doping effect, more impurity levels and stronger phonon scattering respectively. Hence, its maximum *ZT* value of 0.44 is 2 times higher than that of pure Ag₂Te pellet and 100 times higher than that of pure CNTs buckypaper. This result shows that CNTs/Ag₂Te hybrids can be a promising new type n-type thermoelectric material with mechanical flexibility and acceptable *ZT* values.

ASSOCIATED CONTENT

Supporting Information. Supplementary schematic of ZEM-3 setup for buckypapers and table of laser flash data are available free of charge via the Internet at <http://pubs.acs.org>.

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SUPPORTING INFORMATION

Schematic of ZEM-3 setup, as well as thermal diffusivity and specific heat capacity results were shown in supporting information. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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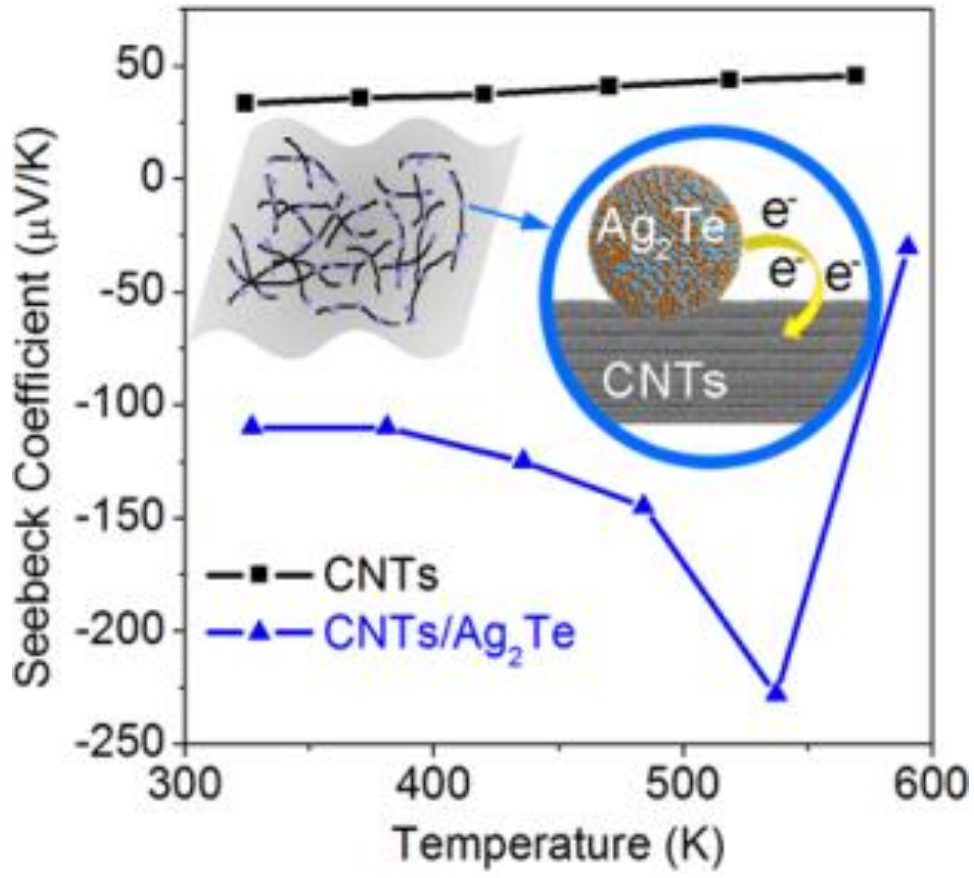
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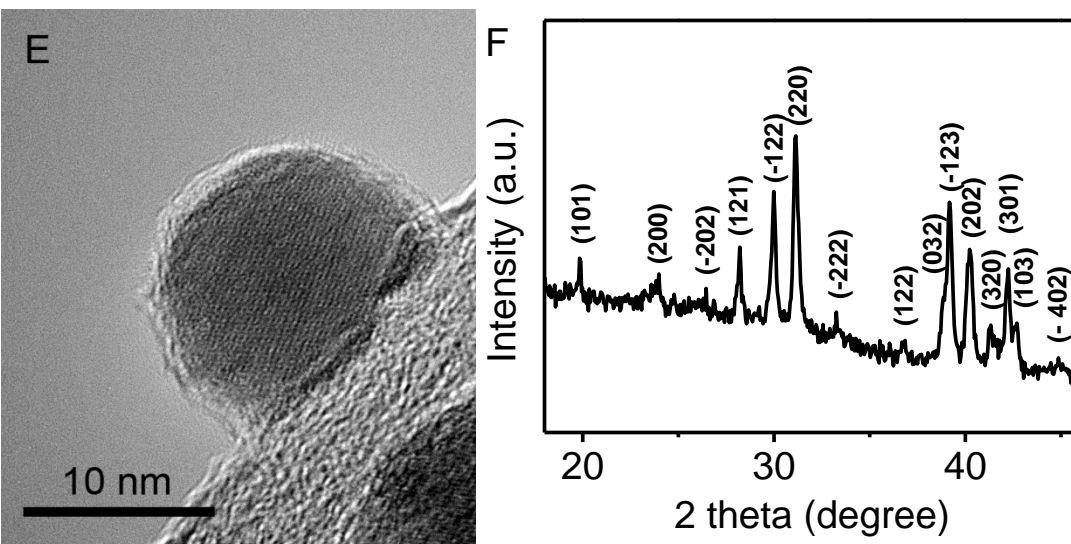
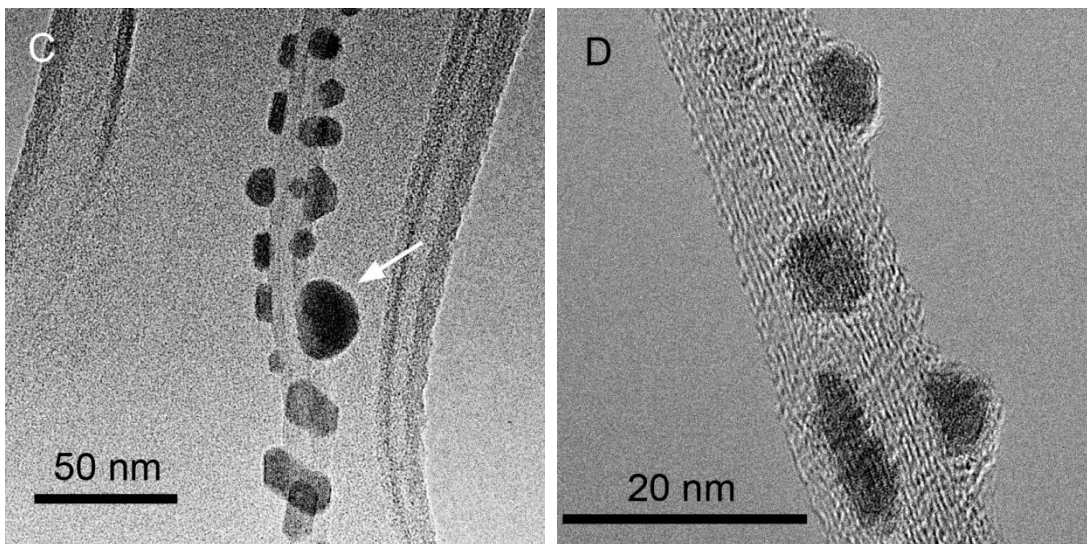
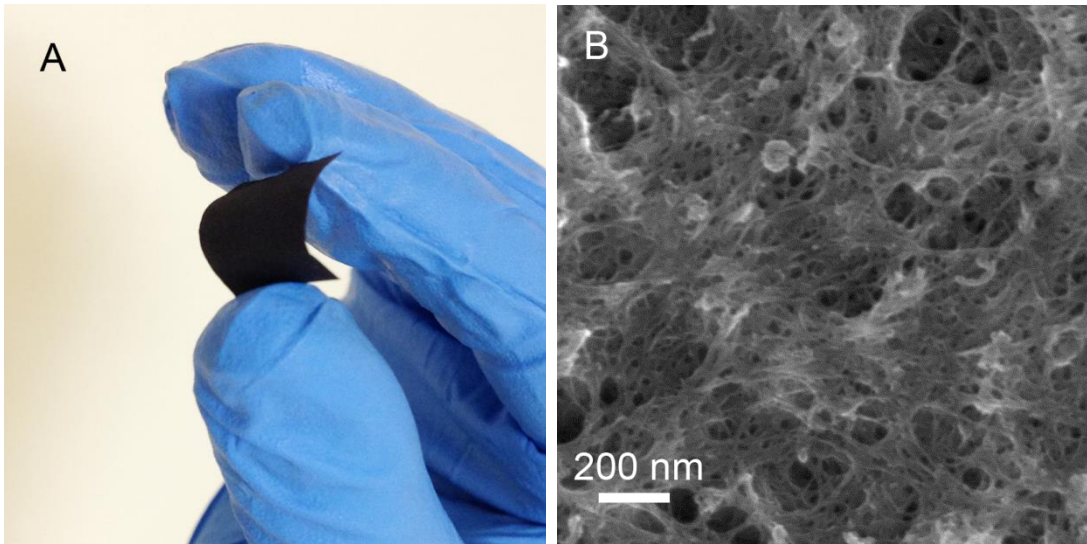


Figure 1. (A) optical image, (B) FESEM image, (C) and (D) TEM images, (E) HRTEM image and (F) XRD pattern of CNTs/Ag₂Te hybrid.

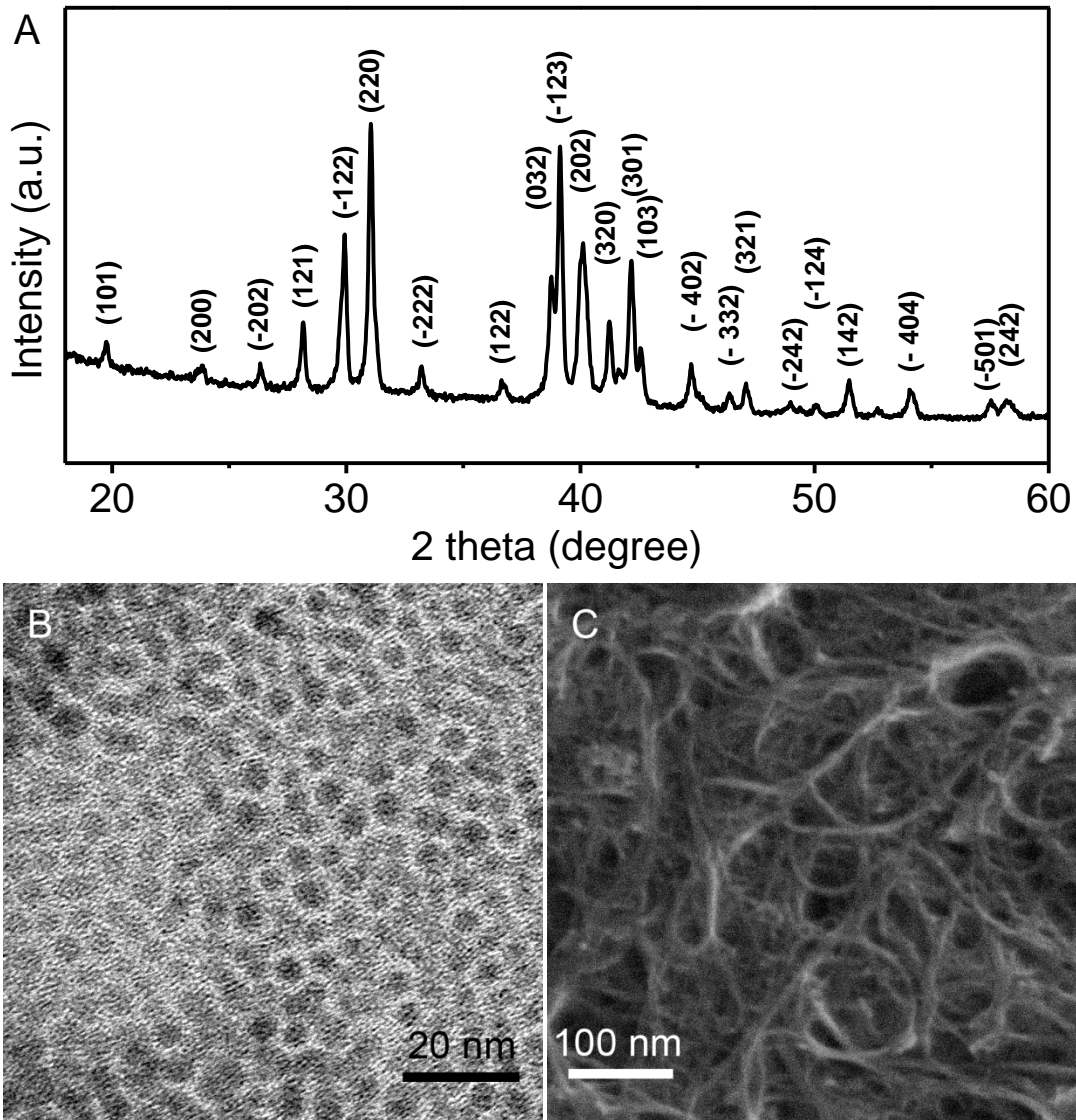


Figure 2. (A) XRD pattern of pure Ag₂Te. (B) TEM image of pure Ag₂Te nano particles. (C) SEM image of pure CNT random networks.

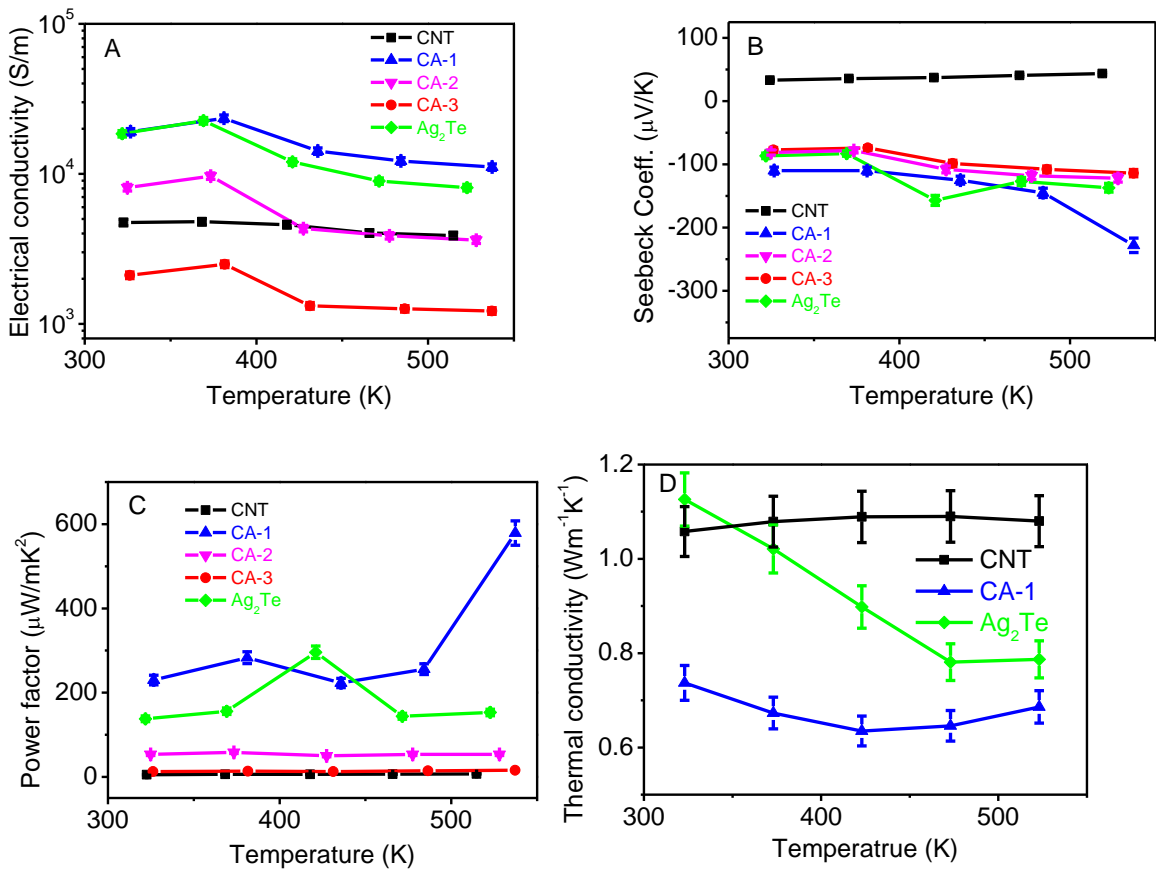


Figure 3. (A) Electrical conductivity, (B) Seebeck coefficient, (C) power factor and (D) thermal conductivity of CNTs/Ag₂Te hybrid buckypapers, pure Ag₂Te pellet and pure CNT buckypaper.

Table 1: Electrical conductivity, carrier concentration and mobility of CNTs/Ag₂Te hybrids and pure Ag₂Te

	σ (S/m)	n (cm ⁻³)	μ (cm ² V ⁻¹ s ⁻¹)
CA-1	1.91×10^4	6.59×10^{18}	181.1
CA-2	8.10×10^3	2.05×10^{18}	246.7
CA-3	2.11×10^3	1.09×10^{18}	120.7
Ag ₂ Te	1.85×10^4	9.10×10^{19}	12.7

N-type CNTs/Ag₂Te Nanohybrid Buckypaper with High Thermoelectric Figure-of-merit

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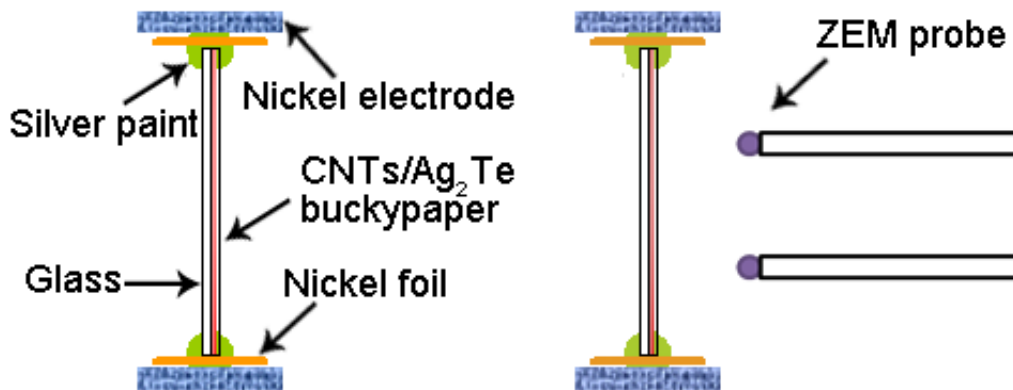


Figure S1. Schematic of ZEM-3 setup for buckypaper measurements.

Thermal conductivity was calculated by $\kappa = \alpha \cdot C_p \cdot \rho$, where κ is thermal conductivity, α is thermal diffusivity, C_p is specific heat capacity, and ρ is density. Thermal diffusivity can be measured by laser flash technique and specific heat capacity can be determined by comparative method. Densities of CNTs/Ag₂Te hybrid buckypaper, pure Ag₂Te pellet and pure CNT buckypaper are 3.51, 7.75 and 0.52 g/cm³ respectively.

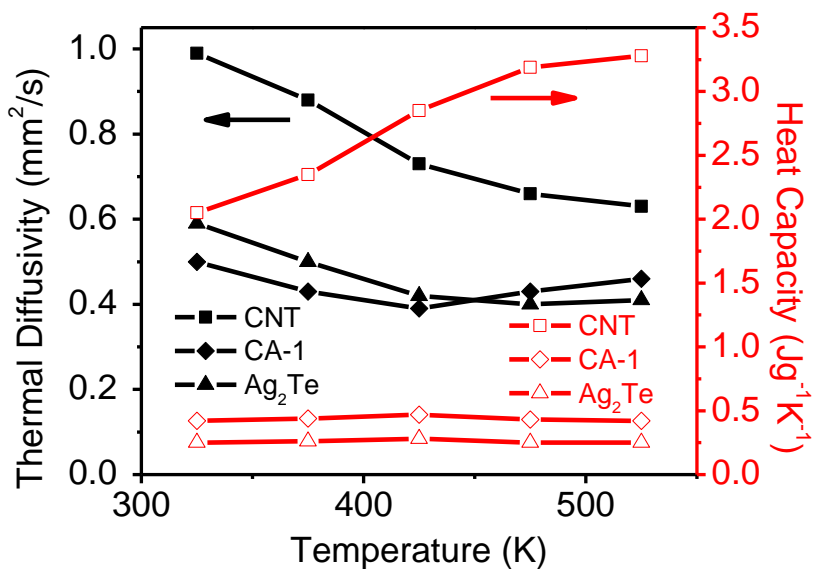


Figure S2. Thermal diffusivity and heat capacity of CNTs/Ag₂Te hybrid buckypaper, pure Ag₂Te pellet and pure CNT buckypaper.