

# Influence of nanoparticles on thermoelectric properties of organic composites

K. Choi, Y. Ryu, J. C. Grunlan, C. Yu\*  
Department of Mechanical Engineering  
Texas A&M University  
College Station, Texas 77843 USA  
\* Corresponding author ([chyu@tamu.edu](mailto:chyu@tamu.edu))

**Keywords:** *Thermoelectrics, Carbon nanotubes, conductive polymer, metal nanoparticles*

## 1. Introduction

Low thermal conductivity of polymeric materials is promising for thermoelectric applications, but their low electrical conductivities and the Seebeck coefficients (thermopowers) have excluded them as a feasible candidate in the past. Here, nanomaterial-polymer composites bring their electrical properties into degenerate-semiconductor or metallic regimes by incorporating conductive fillers into a polymer matrix. The nanocomposite samples were prepared by mixing the emulsion type of polymer and carbon nanotubes (CNTs) together. Then the solution was dried to make a network structure of polymer and CNTs. These polymer composites are adequate for thermoelectric material because the junctions between nanotubes are good for electron transport, but not adequate for phonons. In this type of polymer composite, the stabilizers have important role for energy transport between junctions. The effects of stabilizers were revealed by replacing the different types of stabilizers and altering mixed amount [1-3]. Gold particles were introduced to increase the electrical conductivity of the nanocomposites by increased carrier concentration [4]. The influence of CNTs concentration and proper ratio of CNTs, gold particles and stabilizer on thermoelectric properties were also studied to figure out the maximum electrical properties. The electrical conductivity of the composites was increased over  $10^5$  S/m with a thermopower of typical CNTs and a thermal conductivity of typical polymers. Furthermore, different kinds of metal particles can be applied in order to increase the Seebeck coefficient rather than electrical conductivity in the future. The results show polymers can be viable for thermoelectric energy conversion, replacing heavy and toxic materials such as Bi-Te alloys in the future.

## 2. Material synthesis

Purified single walled carbon nanotubes (SWNTs) were purchased from Unidym, which were used as conductive fillers in the polymer composites. First, SWNTs and Chloroauric acid ( $\text{HAuCl}_4$ ) were mixed with 1~2 ml of deionized water. This aqueous solution was sonicated with Misonix Micron XL2000 Ultrasonic Homogenizer (Misonix, Inc) for 10 min at 50W. Then a stabilizer, PEDOT:PSS (Poly (3,4-ethylenedioxythiophene)poly(styrenesulfonate)) (CLEVIOS PH1000, H. C. Starck), was added with appropriate ratio with SWNTs, in order to make hydrophilic SWNTs. The solution was again sonicated for another 15 min to obtain uniform and well dispersed water base SWNTs and  $\text{HAuCl}_4$  solution. A poly (vinyl acetate) (PVAc) homopolymer emulsion (Vinnapas 401) was then added to the SWNT/Au/PEDOT:PSS mixture and sonicated for 10 min. The total weight including water is typically 25g. All the concentrations of the materials were based on total dry volume of the composite, which were comprised of SWNTs, gold, PVAc emulsion, and PEDOT:PSS. Prepared well dispersed aqueous solution was then poured into a 26 cm<sup>2</sup> plastic container, and dried for 48~72 hours under ambient condition in a fume hood at room temperature. After fully dried, film type composite was baked at 80°C for 2 hours because it was revealed that high temperature drying helps making strong binding between SWNTs and polymer matrix, and removing micro voids in the network structure in our previous work [1]. Finally, fully dried composites were put into a vacuum desiccator for 24 hours in order to completely remove residual water from the composite.

### 3. Result and discussion

In this research, the concentration of SWNTs and polymer emulsion were fixed as 60 vol% and 10 vol%, respectively. The ratio of PEDOT:PSS and Au were changed from 10 vol% and 20 vol%, within 30 vol% of rest of the volume in the composite. Gold nanoparticles were spontaneously reduced on nanotubes because the reduction potential of gold is larger than those of nanotubes as shown in a schematic diagram (Fig. 1.A). A transmission electron micrograph (TEM) shows gold nanoparticles with a polygonal shape were decorated on nanotube bundles (Fig. 1.B). In Fig. 1, the structures of SWNT/Au/polymer composites were shown in scanning electron microscopy (SEM) images. The diameter of SWNTs was 0.8~1.2 nm and the lengths were distributed from 100 to 1000 nm. In Fig. 1.C and 1.D, the SWNTs were well composing uniform nanostructure with polymer binders. With increased Au composition of 20 vol%, the gold particles are shown in Fig. 1.D. Most of SWNTs were wrapped in polymers, and 50~200 nm diameter of gold particles are placed on the surface of polymer wrapped SWNT bundles.

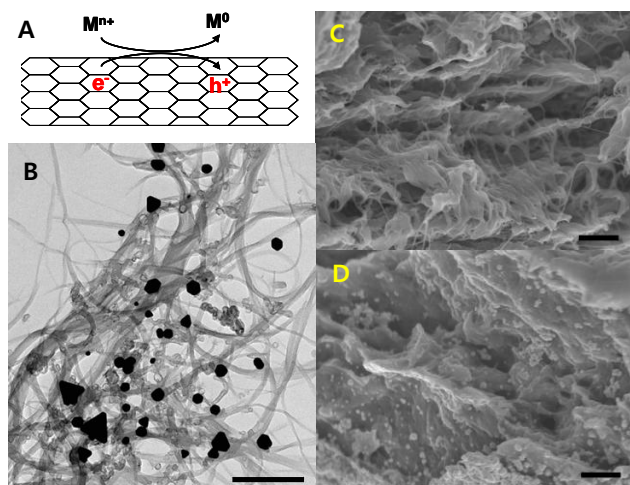


Fig.1. Schematic of Spontaneous reduction for metal nanoparticle decoration on carbon nanotube surface (A). Au nanoparticles (dark) attached to nanotube bundles (wavy lines) (B). SEM images of 10% (C), 20% (D) of gold nano particles in the composites. Scale bar in (B) is 200 nm, and scale bars in (C) and (D) are 1  $\mu$ m.

Fig. 2 shows the electrical conductivity of samples with 10 vol%, and 20 vol% of Au in SWNTs/Au/polymer composites. The electrical conductivity reaches 254,420 S/m at 10 vol% of PEDOT:PSS and 20 vol% of Au with 60 vol% of SWNTs. Note that this value is much larger than other polymer base CNT composites [5, 6]. The electrical conductivity was increased at 10 vol% of Au, but started to decrease at 20 vol% of Au. Au was introduced in this system in order to increase the electrical conductivity by increasing the carrier concentration of the system. We previously investigated the change of electrical properties when gold nanoparticles are decorated on SWNT thin films by immersing the films into gold chloride solution [4]. Au incorporated SWNTs will have more hole carriers because of electron depletion from SWNT to Au, since the work function of SWNTs is smaller than that of Au [7, 8]. According to this theory, the electrical conductivity should be increased with increasing Au contents, which is different from our experimental results. This is due to less amount of conductive stabilizer, PEDOT:PSS, accompanied with the increase of the Au concentration. The effect of PEDOT:PSS was already investigated in our previous work [1, 2].

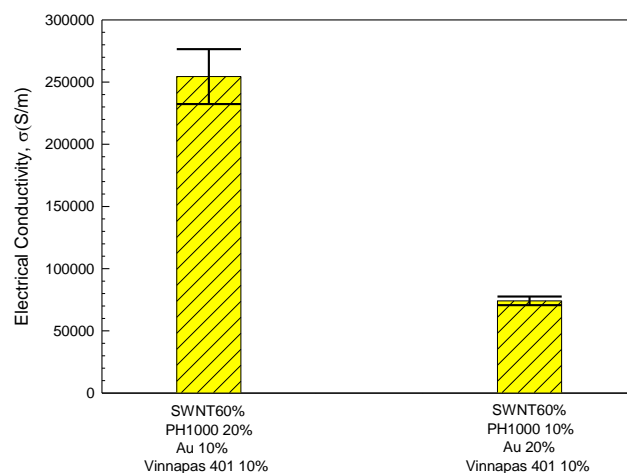


Fig 2. Electrical conductivity as a function of Au concentration in CNT/Au/polymer composites.

The thermoelectric properties of the SWNT/polymer nanocomposites can be manipulated by conductive stabilizer due to the filtering effect of junctions for electron hopping. Insufficient stabilizers often make non-uniform SWNTs/Au/polymer structure. When

SWNTs are not well dispersed due to a lack of stabilizers, then the network structure is not uniform. From the SEM images in Fig. 1, the nanostructure of the 20 vol% Au (Fig. 1.D) was not uniformly distributed, when compared to that of Fig. 1.C. In Fig. 1.C, SWNTs were not uniformly dispersed due to insufficient stabilizer. From this experiment, it is clearly shown that the uniformity of SWNT/Au/polymer structure is critical factor for electron transport properties, rather than the ratio of contents.

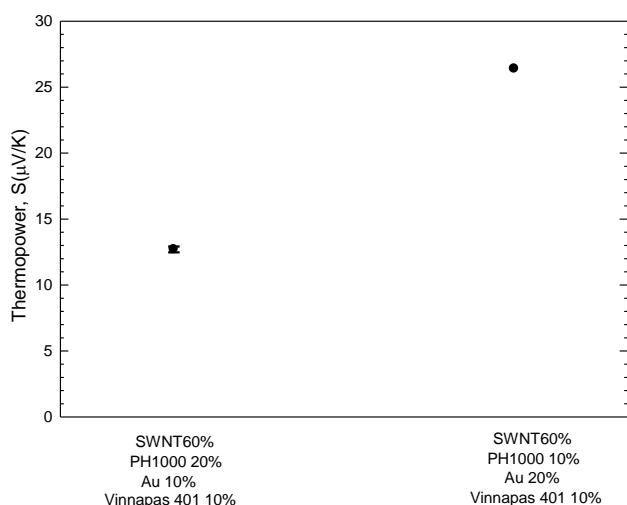


Fig.3. Thermopower as a function of gold concentration.

Thermopower is shown in Fig. 3 when the ratio of Au to PEDOT:PSS was changed. The thermopower was varied from 12.7 to 26.4 μV/K, following the general trend of thermopower and electrical conductivity in bulk materials (decreasing thermopower with increasing electrical conductivity, and vice versa). These values are lower than our previous research (40~60 μV/K [1]) due to introducing Au whose thermopower is lower than SWNTs (1.94 μV/K at room temperature [9]). Power factors ( $S^2\sigma$ ) of these samples are plotted in Fig. 4.

In conclusion, the effect of Au and PEDOT:PSS contents on thermoelectric behavior of SWNT/Au/polymer composites was studied in this report. The electrical conductivity, the Seebeck coefficient and the power factor were measured and analyzed as a function of different contents of PEDOT:PSS and Au at room temperature. The electrical conductivity was dramatically enhanced to

~200,000 S/m by incorporating gold nanoparticle into SWNT/polymer nanocomposite while thermopower was not very sensitive to Au contents. Another critical factor for electrical conductivity was the ratio of SWNT to PEDOT:PSS.

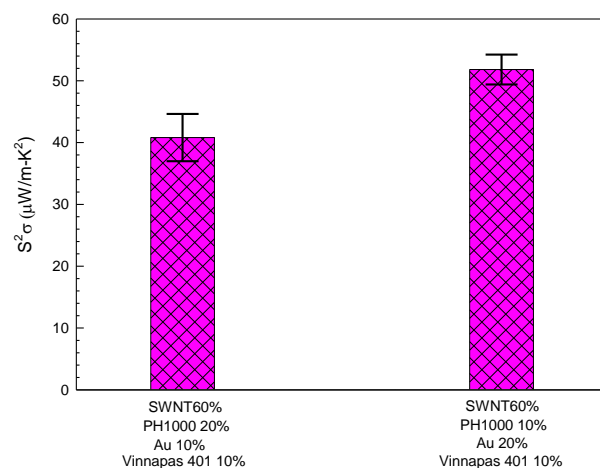


Fig.4. Power factor as a function of gold concentration.

With insufficient PEDOT:PSS for nanotube dispersion, the electrical conductivity was low due to non uniform distribution of SWNTs. In this study, the best volume composition of PEDOT:PSS and Au with 60 vol% of SWNT were respectively 20 vol% and 10 vol%, which means that the balance of stabilizer and carrier source is critical factor for this type of SWNT/polymer composite. The maximum power factor reaches 52 μW/mK<sup>2</sup> at room temperature, and this value is much higher than those of other polymer based thermoelectric materials. By incorporating other metals to SWNTs/polymer composites, the potential of this approach can provide feasible method to synthesize effective thermoelectric materials.

#### Acknowledgment

The authors gratefully acknowledge financial support from the US Air Force Office of Scientific Research (Grant No. FA 9550-09-1-0609) under the auspices of Dr. Charles Lee.

## References

- [1] D. Kim., Y. S. Kim, K. Choi., J. C. Grunlan, C. Yu “Improved Thermoelectric Behavior of Nanotube-Filled Polymer Composites with Poly (3,4-ethylenedioxythiophene) Poly(styrenesulfonate)”. *ACS Nano*, Vol 4, pp. 513–523, 2010.
- [2] C. Yu, Y. S. Kim, D. Kim, J. C. Grunlan “Thermoelectric Behavior of Segregated-Network Polymer Nanocomposites”. *Nano letter*, Vol 8, pp. 4428–4432, 2008
- [3] Y. S. Kim, D. Kim, K. J. Martin, C. Yu, J. C. Grunlan “Influence of stabilizer concentration on transport behavior and thermopower of CNT-filled latex-based composites”. *Macromolecular Materials and Engineering*. 295, pp. 431-436, 2010
- [4] C. Yu, Y. Ryu, L. Yin, H. Yang, “Modulating electronic transport properties of carbon nanotubes to improve the thermoelectric power factor via nanoparticle decoration”, Vol 5, pp. 1297–1303, 2011
- [5] Q. Yao, L. Chen, W. Zhang, S. Liufu, X. Chen, “Enhanced Thermoelectric Performance of Single-Walled Carbon Nanotubes/Polyaniline Hybrid Nanocomposites”. *ACS Nano*, Vol 4, pp. 2445–2451, 2010
- [6] C. Meng, C. Liu, S. Fan, S. Liufu, “A Promising Approach to Enhanced Thermoelectric Properties Using Carbon Nanotube Networks”. *Adv. Mater.* Vol 22, pp. 535–539, 2010
- [7] M. Shiraichi, “Work function of carbon nanotubes”. *Carbon*. Vol 39, pp. 1913–1917, 2010
- [8] J. C. Riviere, “Work function of gold”. *Appl. Phys. Lett.* Vol 8, pp. 172, 1966
- [9] D. W. Rowe, “*CRC handbook of Thermoelectrics*”, CRC Press, Boca Ranton, FL, pp. 390. 1995