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Ultrafast Photoconductivity Measurements of a Thermoelectric Nanocomposite: Tellurium Nanowire/PEDOT:PSS

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Abstract

This project explores the conductivity properties of a novel thermoelectric hybrid material (Tellurium nanowires in a conducting polymer PEDOT:PSS) using both static and time-resolved conductivity measurements. We find that the effect of the conducting polymer PEDOT is weak and that the observed differences in conductivity measurements between the hybrid and non-hybrid material are most likely caused by the different sizes of the nanowires.

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Cover Page Footnote
Thank you to Professor James Heyman for advising this research project. I would also like to thank Macalester College and the National Science Foundation for providing the workspace and the funding for this project.

Ultrafast Photoconductivity Measurements of a Thermoelectric Nanocomposite: Tellurium Nanowire/PEDOT:PSS

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I. INTRODUCTION

Thermoelectric materials convert the flow of heat directly into electric current. They are used to make solid-state heat engines and refrigerators. There are a variety of different types of materials involved in thermoelectric research. Many consist of naturally occuring minerals that have been altered or added to another type of material (to form a composite) to improve efficiency. There is an increasing demand to make improvements to the efficiency of thermoelectric materials because of their applications to fields such as energy production and conservation. A novel thermoelectric material (TeNW/PD, an organic/inorganic hybrid) has shown promise for thermoelectric applications.

The effciency of a thermoelectric device is measured by the figure of merit ZT.

$$ZT = \frac{S^2 \sigma T}{k} \tag{1}$$

where S is the Seebeck coefficient (or thermo power), σ is the electrical conductivity, T is the temperature, and k is the thermal conductivity. To optimize ZT we want to maximize electrical conductivity at higher temperatures while mantaining a low thermal conductivity[5]

Bare tellurium nanowires have a low electrical conductivity ($.1 Scm^{-1}$), but a high thermopower ($400 \mu V K^{-1}$)[35], therefore adding a polymer such as PEDOT:PSS (which has a smaller thermopower but greater electrical conductivity) create a more efficient thermoelectric hybrid material. Recent studies have shown that the electrical conductivity of the hybrid material TeNW/PD is greater than that of each of the components separately[4].

Recent work by the Heyman research group explored the steady state electrical properties of this material using THz and infrared transmission measurements[1]. My research continues to explore conductivity changes of this material using static and time-resolved conductivity measurements.

II. METHODOLOGY

A. Samples

We examined two materials consisting of tellurium nanowires coated with the conducting polymer PEDOT:PSS. The first sample (TeNW/PD) is an organic/inorganic composite with crystalline tellurium nanowires dropcast on a quartz substrate and coated with PEDOT:PSS, see Figure 1. These nanowire have radius of 40 nm and length of 500 nm.

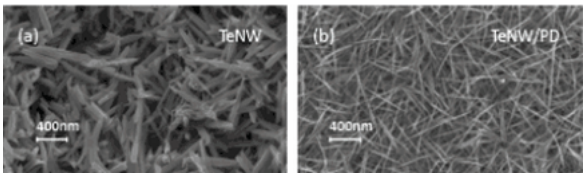


FIG. 1. (a) the Scanning Electron Microscope (SEM) image of the bare tellurium nanowire sample (TeNW), (b) the SEM image of the tellurium nanowire sample coated in PEDOT:PSS (TeNW/PD)

The second sample (TeNW/PD-N) was prepared in two steps. We started with a sample of crystalline tellurium nanowires dropcast on quartz substrate. These nanowires have radius of 100 nm and length of 600 nm. X-ray diffraction measurements show tellurite peaks indicating that the bare tellurium wires are oxidized, therefore we etched the sample with an HCl dilution to strip it of its oxide. Then we coated the etched sample with PEDOT:PSS using a spin-coater.

We also investigated a bare tellurium nanowire sample (TeNW) that is identical to that used in the creation of our TeNW/PD-N sample, see Figure 1. Therefore its nanowires are of the same size, radius of 100 nm and length of 600 nm.

A sputtered tellurium film sample (Sput Te) was also investigated. It is a polycrystalline film of tellurium deposited on quartz by sputtering. It is 220 nm thick, with a grain size of about 70nm.

B. Experimental Process

We used time-resolved conductivity measurements to study the conductivity properties of our samples. These measurements are done by optically exciting the samples with a pulse of light and then measuring the resulting change in conductivity. The XL-500 system (Figure 2) measures the change in transmission versus time (as seen in Figure 5), with a 200 femtosecond resolution, of the Terahertz pulse after photoexcitation of the sample. We are able to measure the change in transmission because it is directly related to the change in conductivity of the sample. These conductivity measurements are time-resolved therefore there is no contact or wires connected

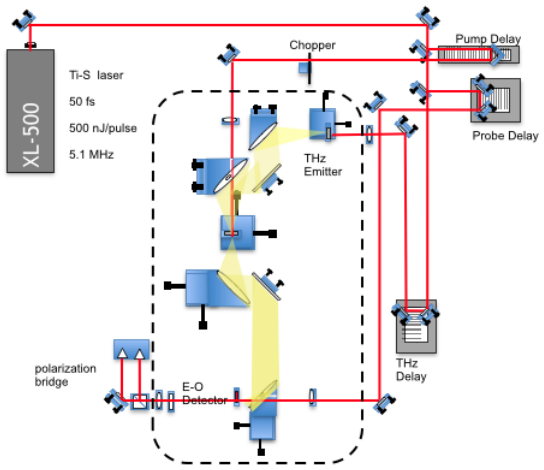


FIG. 2. A diagram of the layout of the Optical Pump/THz Probe experiment. The THz transmission experiment has the same layout but without the pump beam.

to the sample.

Our measurement allows us to directly measure the waveform (electric field amplitude versus time) of the THz pulses. We obtain the spectrum (electric field amplitude versus frequency) by taking a Fourier Transform of the waveform. The ratio of the spectrum of a pulse transmitted through our sample to one transmitted through a reference sample determines the transmission of the sample as a function of frequency. The transmission determines the conductivity[1].

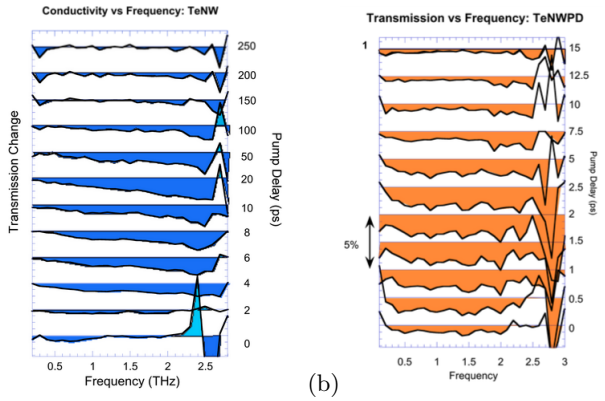


FIG. 3. (a) The change in transmission as a function of frequency (THz) and time (ps) for sample TeNW. (b) The change in transmission as a function of frequency (THz) and time (ps) for sample TeNW/PEDOT. The artifact near $f = 2.7THz$ is the tellurium optical phonon line.

We also use the Optical Pump/THz Probe following photo-excitation measurements to measure the change in transmission and study carrier dynamics of the material. The samples were optically pumped with a 100nJ, 50fs pulse from a FemtoLasers XL-500 Ti:Sapphire Laser (XL-500 system) and probed with a pulse of terahertz (THz) radiation. With this technique we photoexcite the free carriers in a material with the pump beam and then use the THz probe to monitor the evolution of the conductivity, which dictates the transmission of the THz pulse through the sample. In this way we measured the change in conductivity of our samples versus time after photoexcitation with a time resolution of 200 femtoseconds.[1].

III. DISCUSSION

The THz conductivity measurements showed the carrier cooling time (the time of increase in the sample's conductivity) and the photoconductivty decay time (the time it takes for the sample's conductivity to decay to its original value) for each sample. Following photoexcitation, the sample conductivity increases, approaching a higher value over time (τ_c), the conductivity then decays to its original value over time (τ_R). We observe that the photoconductivity decay time of TeNW/PD is much shorter than the decay time of TeNW and TeNW/PD-N (See table below and Figure 4).

Sample	**Photoconductivity Decay Rate (ps)**	**Carrier Cooling Time (ps)**
TeNW/PD	1.39	6.80
TeNW/PD-N	2.63	130.5
TeNW	2.56	97.20

In the Optical Pump/THz Probe measurements we observe a similar pattern among the three samples in the time frame immediately following photoexcitation. After photoexcitation ($10ps$), each sample shows immediate decrease in change in transmission (photoexcitation decay time) and then exhibits a longer recovery period (carrier cooling time). The transmission change induced by the pump is described as

$$\langle \Delta T \rangle = T_0(1 - e^{-t/\tau_C})e^{-t/\tau_R} \qquad (2)$$

where τ_C is the carrier cooling time and τ_R is the conductivity decay time, which is controlled by the free carrier trapping and recombination. We observe that the photoconductivity decay time is strongly influenced by the characteristics of each sample. We also see that the carrier cooling time varies significantly among samples. These results suggest that the density of traps and recombination centers at the nanowire surfaces has an effect on the conductive properties of the material.

Our principle result is that the photoconductivity decay time is much shorter in TeNW/PD than our other samples, which indicates that the decay time is dependent on recombination and trapping at the nanowire surfaces.

The diameter of the nanowires has little effect on the magnitude of conductivity change and the carrier cooling

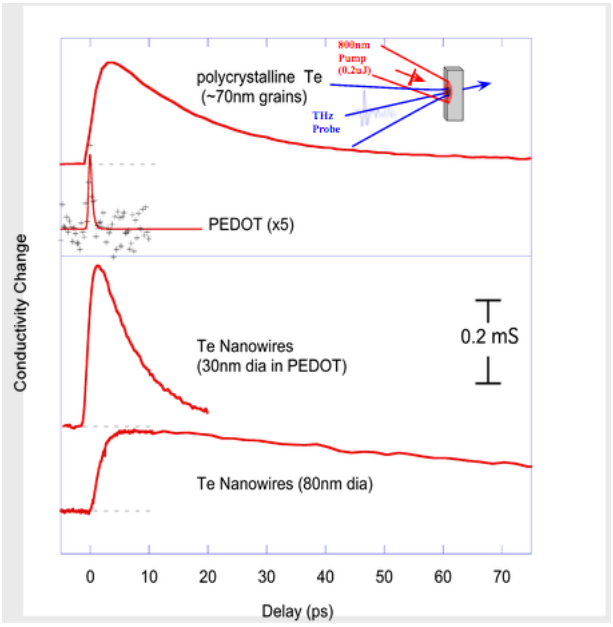
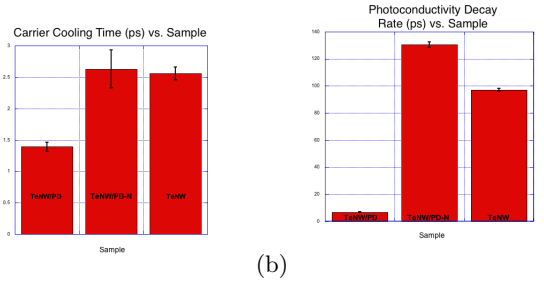


FIG. 4. Photoexcitation causes increase in photoconductivty for all samples. TeNW/PD shows a much smaller response than TeNW and Sput Te, with photoconductivity decaying within 1ps of photoexcitation.



(a) (b)

FIG. 5. (a) The carrier cooling time (ps) for each sample. (b) The photoconductivity decay time (ps) for each sample. The significant difference between the decay time of TeNW/PD and TeNW/PD-N, TeNW suggests that PEDOT:PSS is *not* the reason for conductivity differences between the samples.

time, but a strong effect on the photoconductivity decay time. We also conclude that the effect of the PEDOT surrounding the nanowires is weak.

We also observed that the angle between the polarizations of the pump and THz beam strongly influence the signal. We expect that the photoexcitation should only effect the THz conductivity parallel to the nanowire axis, and that nanowires absorb pump beam radiation that is parallel to the nanowire axis. We expect that the change in transmission is as follows:

$$\langle \mid \Delta T \mid \rangle \propto \frac{1}{2}(1 + cos^2\theta) \tag{3}$$

where $\langle \mid \Delta T \mid \rangle$ represents the measured change in transmission, and θ represents the angle between the pump and Terahertz beam.

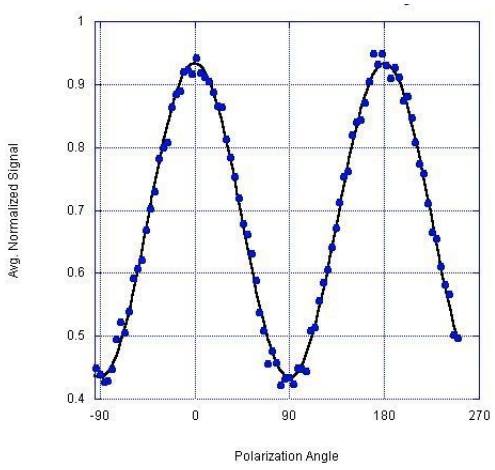


FIG. 6. Tranmission change versus polarization angle between pump and THz beams for TeNW/PD. The solid line is our model in Equation 3.

The obvious fit between our data and the model in Figure 6 suggest that the time-resolved signal is dominated by photoconductivity in the nanowires[1].

IV. CONCLUSION

In this project we studied a novel thermoelectric material of tellurium nanowires coated with conducting polymer PEDOT:PSS by using Terahertz and Optical Pump/Terahertz Probe measurements to characterize the conductivity as a function of frequency and the change in transmission as a function of time, respectively. Our results show that the change in conductivity of our samples after photoexcitation is dominated by the photoconductivity of the tellurium wires. We find that the PEDOT:PSS matrix does not strongly effect the decay of the photoconductivity. Instead, we have strong, indirect evidence that the diameter of the nanowires controls this rate. This suggests that recombination occurs at nanowire surfaces because the narrower nanowires have shorter photoconductivity decay times[2].

This also gives the scientific community insight into how the method of sample synthesis effects the thermoelectric material's efficiency. Future work could potentially be researching the optimum length and diameter of tellurium nanowires used in these samples. It would also be worth while to understand the most effective method in which to create these samples.

1. Citations

[1]J. N. Heyman, A. Sahu, N. E. Coates, B. Ehmann, J. J. Urban *Carrier Lifetime Enchancement in a Tellurium Nanowire/PEDOT:PSS Nanocomposite by Sulfur Passivation*, Materials Research Library Online Proceedings (to be published).

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[3]Alebachew, Banteaymolu (2013) *Electrical Conductivity of Tellurium nanowires on PEDOT:PSS* Macalester Journal of Physics and Astronomy: Vol. 1: Iss. 1, Article 2.

[4]Kevin C. See, Joseph P. Feser, Cynthia E. Chen, Arun Majumdar, Jeffrey J. Urban, and Rachel A. Segalman *Water-Processable PolymerNanocrystal Hybrids for Thermoelectrics* 10 (11), 4664-4667 (2010).

[5]Christopher J. Vineis, Ali Shakouri, Arun Majumdar, and Mercouri G. Kanatzidis *Nanostructure Thermoelectrics: Big Efficiency Gains from Small Features* Advanced Materials 22, 3970-3980 (2010).