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## Electrical Conductivity of Tellurium nanowires on PEDOT:PSS

### Abstract

The purpose of this project is to understand the electrical conductivity and infrared absorption spectrum of a hybrid material between Tellurium nanowires and a carbon polymer called PEDOT:PSS. This hybrid material shows much higher conductivity than its components and this behavior gives a great promise for thermoelectric effect. The most intriguing property of this material is observed when taking absorption spectrum from far to near infrared. The hybrid material shows a much bigger absorption edge than Te NW. This project attempts to explain this shift using the confinement energy model and Fermi blocking (due to doping). The result from these two models shows that the absorption can be best explained using the Fermi blocking model in which the hybrid material acts as a highly doped semiconductor. This result might be useful to understand its behavior further by controlling the amount of PEDOT:PSS in the hybrid.

### Cover Page Footnote

Advisor : Professor James Heyman Physics and Astronomy Department Macalester College

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*Macalester College*

May 2, 2013

## **Abstract**

The purpose of this project is to understand the electrical conductivity and infrared absorption spectrum of a hybrid material between Tellurium nanowires and a carbon polymer called PEDOT:PSS. This hybrid material shows much higher conductivity than its components and this behavior gives a great promise for thermoelectric effect. The most intriguing property of this material is observed when taking absorption spectrum from far to near infrared. The hybrid material shows a much bigger absorption edge than Te NW. This project attempts to explain this shift using the confinement energy model and Fermi blocking (due to doping). The result from these two models shows that the absorption can be best explained using the Fermi blocking model in which the hybrid material acts as a highly doped semiconductor. This result might be useful to understand its behavior further by controlling the amount of PEDOT:PSS in the hybrid.

# I Introduction

Thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa. This effect is well studied and started in 1820 by German scientist Thomas Johann Seebeck. Seebeck found that a circuit made from two dissimilar metals, with junctions at different temperatures would deflect a compass magnet. Seebeck initially believed this was due to magnetism induced by the temperature difference and thought it might be related to the Earth's magnetic field. However, it was quickly realized that a "Thermoelectric Force" induced an electrical current, which by Ampere's law deflects the magnet. More specifically, the temperature difference produces electric potential (voltage) which can drive an electric current in a closed circuit. Today, this is known as the Seebeck effect and typically has a unit of  $\frac{\mu V}{K}$  [3].

However different devices have different ability to change temperature differences into thermovoltage. This ability is measured by the thermoelectric figure of merit  $ZT$  (Figure of merit  $Z$  multiplied by  $T$ ).  $ZT$  is used to characterize thermoelectric performance of a device[1].

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

Where  $\sigma$  is electrical conductivity,  $S$  is thermopower and  $k$  is thermal conductivity. As shown in equation (1), the thermal figure of merit  $ZT$  increases as function of the Seebeck effect  $S$  and electrical conductivity  $\sigma$  and decreases as a function of thermal conductivity  $k$ . Unfortunately, these variables cannot be independently controlled, and the resulting trade-offs severely limit  $ZT$  to a value several times, lower than the practical requirements, with the best known material tellurides of bismuth ( $Bi_2Te_3$ ) having only  $ZT \sim 1$ . For instance materials such as metals have higher electrical conductivity, however, due to lower Seebeck effect and much higher thermal conductivity they have low thermoelectric figure of merit  $ZT$ . In most inorganic materials,  $S$ ,  $\sigma$ , and  $k$  are degenerate. To illus-

trate this, consider increasing the electrical conductivity of a semiconductor by doping the material and therefore increasing the carrier concentration. By doing this, the electrical conductivity increases but thermopower decreases as there is less asymmetry in the distribution of charge carriers. Similarly in the denominator, the thermal conductivity will also increase as the electronic component of the thermal conductivity increases. In this manner all three material properties are in competition with one another making decoupling or simultaneous optimization of these properties difficult. This phenomena can be explained using a triangle as in Figure 3.

However on the basis of equation 1, electronically conductive organic polymers are interesting candidates for thermoelectric materials since their  $k$  values of  $0.05 - 0.6 \text{ W m}^{-1} \text{ K}^{-1}$  at room temperature are an order of magnitude or more lower than the values for crystalline thermoelectric materials such as tellurides of bismuth, and their  $\sigma$  values are adjustable from metallic to semiconducting values depending on doping [4]. One good example of these polymers is Te nanowire doped with PEDOT:PSS.

A conducting poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is conjugated polymer produced from PEDOT and PSS as shown in Figure 1. PEDOT:PSS as a conjugated polymer has three  $sp^2$  orbitals out of which two  $sp^2$  orbitals form the  $\sigma$  bond (stable and strong). The third  $sp^2$  orbital ( $P_z$ ) form the  $\pi$  bond. This bond is weak and results in electron de-localization. Hence the  $\pi$  bonds are responsible for conduction in PEDOT:PSS. This polymer is also p-type by nature [2]. Even though PEDOT:PSS is the most widely used conducting polymer, full understanding of charge transfer mechanism is still lacking [2]. However the dominant charge transfer mechanism in conducting PEDOT:PSS is thought to be hopping conduction. Films of PEDOT:PSS are considered to consist of a phase-segregated material consisting of about 25 nm wide lentil shaped PEDOT:PSS grains surrounded by a nanometer-thick shell formed by PSS[1]. The resulting conductivity is therefore strongly dependent on variations in this morphology in that the

hopping conduction occurs between carbon nanotubes. The thermoelectric properties of PEDOT:PSS have been widely studied. PEDOT:PSS like many other polymers has much lower thermal conductivity ( $0.2 - 0.3 \text{ W m}^{-1} \text{ K}^{-1}$ ) but exhibit the same competing trends with  $S$  and  $\sigma$ . Even though PEDOT:PSS has small thermopower  $S$  compare to other polymers, as a conducting polymer it has a much higher electrical conductivity  $\sigma$  which is in the order of  $80 \text{ S cm}^{-1}$ . This gives a much higher  $S^2\sigma$  and hence greater figure of merit  $ZT$  at room temperature.

Tellurium nanowires on the other hand have lower electrical conductivity (in the order of  $0.1 \text{ S cm}^{-1}$ ) as compared to PEDOT:PSS but has a much higher thermopower ( $S \sim 400 \mu \text{ V K}^{-1}$ ) as shown in Figure 7. These nanowires also exhibit lower thermal conductivity  $k$  but higher than the thermal conductivity of PEDOT:PSS.

In recent research at the University California Berkeley [3], have shown that a hybrid bulk network (i.e., interdigitated nanowires forming a haystack) of crystalline tellurium nanowires can be coated in a conducting polymer, PEDOT:PSS. This material was first synthesized by See et al [3]. who observed that the electrical conductivity of the hybrid material was greater than either of the constituent components as shown in Figure 4. This conductivity behavior of the hybrid material became an area of interest to undertake my independent research with Professor James Heyman at Macalester College.

To understand this behavior, infrared absorption, X-ray diffraction and terahertz conductivity measurements were taken. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the transition energy of the bond or group that vibrates. The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction. The X-ray diffraction helps to study the structure of states in a sample. This is important to understand the average spacing between layers or rows

of atoms, to determine the orientation of a single crystal and to measure the size of small crystalline regions.

## II Methodology

The samples for this experiment were obtained from D.r Nelson Coates at Molecular Foundry, Lawrence, Berkeley National Laboratory. The samples include Te nanowires with wire diameter  $d \sim 71\text{nm}$  (Figure 6), PEDOT:PSS (Figure 5), and Te+PEDOT:PSS with wire diameter  $d \sim 30\text{nm}$  (Figure 7).

The first part of the experiment X-ray diffraction (XRD) is designed to observe the concentration of Te nanowires on the Te nanowires sample and Te+PEDOT:PSS sample. The concentration of Te nanowires is then proportional to the integration of the area under each peak of the X-ray diffraction data shown in Figure 10. As shown in Table 1 the peak areas of [100] and [110] lines suggest Te nanowires concentration in the two samples are roughly the same. This suggestion was also supported when we undertook Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS measurements. However, XRD peaks in the Te+PEDOT:PSS sample are broader which indicates lower long range order. This may arise from smaller Te nanowires radius, lower crystallinity, or stress. Peaks for which the third Miller index [101] is non-zero are weak or absent in the the Te + PEDOT:PSS. This may indicate partial orientation of wires on substrate i.e., they might all be laying down.

The second experiment was terahertz conductivity measurement. This measurement is designed so the conductivity behavior of the samples as we increase the frequency.

The last and probably the most important measurement is to undertake infrared absorption of Tellurium nanowires, PEDOT:PSS and the hybrid material Te + PEDOT:PSS. To see a full picture of IR absorption spectrum, far-infrared, mid-infrared and near-infrared

spectrum were taken separately. The results from these measurements were then combined for each sample to give an over all IR absorption trend. It is important to note that the far-infrared, approximately  $400 - 10\text{cm}^{-1}$ , lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid-infrared, approximately  $4000 - 400\text{cm}^{-1}$  may be used to study the fundamental vibrations and associated rotational-vibrational structure. The higher energy near-IR, approximately  $14000 - 4000\text{cm}^{-1}$  can excite overtone or harmonic vibrations. As shown in Figure-8, the hybrid material (Te+PEDOT:PSS) and the individual components have shown different absorption spectrum from the far-infrared to the near infrared.

### III Results and Discussion

The conductivity of a material is complex and can be calculated as in equation 2 below.

$$\tilde{\sigma} = \sigma' + i\sigma'' \quad (2)$$

In most conductive materials, the real part of the conductivity much greater than the imaginary part. For conductive materials, as we increase the frequency the Drude model predicts that the conductivity decreases. This is due to the fact that conduction in conductors is due to the free mobility of electrons. The conductivity measurements undertaken in this experiment as shown in Figure 11 and 12, however, suggests that our samples conductivity are not due to free electron mobility rather due to the vibration of particles. The Te NW as shown in Figure 11, are poor conductors. One important feature to observe here is the the imaginary part of the conductivity is slightly bigger than the real part. This simply implies the material is lossy dielectric material. The conductivity in the hybrid

material, however, has bigger real part as compared to the imaginary part suggests that the material is in fact conductive. However, as the frequency increase the conductivity also increases which shows the conductivity is due to the partially localized electrons or holes. This type of conduction can thought be as a hopping conduction as described in the introduction.

The last and the most important experiment was the IR absorption experiment. As shown in Figure 8, all the materials have shown their vibrational mode in the far infrared spectrum. As the spectrum moves from the FIR to the NIR, each of the materials have shown different behavior. The pure PEDOT:PSS sample shows that its absorption won't be seen until about  $11000\text{cm}^{-1}$ , far deep into the NIR. However, the absorption edge for the Te nanowires occur at about  $0.35\text{eV}$ . This in fact happens to be the band gap energy of Tellurium which explains why we the absorption line. However, what about the hybrid material? Is it due to the Te nanowires or the PEDOT:PSS?

To understand this the pure PEDOT:PSS IR spectrum was subtracted out of the hybrid material so that if the absorption is due to the Te nanowires then the remaining component should line up with the Te NW absorption. However this is not the case as shown in Figure 9. Here, the vibrational mode of the remain spectrum suggests that the vibrational mode seen in Figure 8 was perhaps due to the pure PEDOT:PSS. The interesting behavior is however, the absorption which occurs about  $\sim 0.8\text{eV}$ . This absorption is about  $\sim 0.5\text{eV}$  more than the absorption of Te NW. So the question is then why do we see this absorption? This could be explained using either the confinement energy model or the Fermi blocking ( due to doping) model.

The quantum confinement effect can be observed once the diameter of the particle is of the same magnitude as the wavelength of the electron wave function. When materials are this small, their electronic and optical properties deviate substantially from those of bulk materials. A particle behaves as if it were free when the confining dimension is large

compared to the wavelength of the particle. During this state, the bandgap remains at its original energy due to a continuous energy state. However, as the confining dimension decreases and reaches a certain limit, typically in nanoscale, the energy spectrum turns to discrete. As a result, the bandgap becomes size dependent. The confinement energy is calculated using the following equation.

$$E_T = hf = E_g + E_{electrons}^c + E_{holes}^c \quad (3)$$

$$E_c = E_{electrons}^c + E_{holes}^c = \left(\frac{\hbar\pi}{d}\right)^2 \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \quad (4)$$

Using this model, the total energy would be the absorption edge energy  $\sim 0.8\text{eV}$ . This is then used to predict the size of the crystals in the hybrid material. The result shows the crystals will have to be about  $6\text{nm}$  in diameter to achieve the absorption edge. However, the measured size of the particles is in fact about  $30\text{nm}$ . Therefore this model doesn't seem to explain the absorption edge observed.

The Fermi energy (EF) of a system of non-interacting fermions is the increase in the ground state energy when exactly one particle is added to the system. It can also be interpreted as the maximum energy of an individual fermion in this ground state. The chemical potential at zero temperature is equal to the Fermi energy. In this model the total energy of the system is then calculated as shown below.

$$E_T = hf = E_g + \frac{\hbar^2 k_f^2}{2m_e^*} + \frac{\hbar^2 k_f^2}{2m_h^*} \quad (5)$$

$$k_f = (3\pi n_e)^{\frac{1}{3}} \quad (6)$$

Where  $n_e$  is the concentration of electrons and  $k_f$  is the fermi wave vector. From equation 5 and 6, if we know  $n_e$  we would be able calculate the value of the total energy or vice

verse. In this experiment, the absorption edge of the hybrid material is the total energy  $\sim 0.8\text{eV}$ . From this the concentration of the electrons is calculated to give  $n_e = 10^{19}\text{cm}^{-3}$ . Even though this result seems to be high, it is a reasonable explanation for the conductivity behavior we see. The concentration of electrons is also similar to highly doped silicon.

## IV Summary and Conclusion

Thermoelectric has long been too inefficient and has not been applicable due to materials low performance. However, materials such as Te+PEDOT has shown a better electrical conductivity and very low thermal conductivity which would make this material the best candidate. The conductivity behavior of this hybrid material has been an area of research as it behaves much different from its individual components. This conductivity behavior is not, however, due to free electron mobility in stand it is due to electron delocalization.

The most interesting behavior is seen when we undertake IR measurement which showed that the absorption edge of the hybrid material very different from the individual components. This phenomena can be explained using Fermi blocking (doping) model.

The next step in this project will be study the behavior of the hybrid material by controlling its PEDOT:PSS component. I hope to see that by changing the amount of this carbon polymer component the absorption edge shift would also change and this would give a better understanding of the hybrid's electrical property. Even though I won't be working on this next section anytime soon, my Advisor professor James Heyman has planned to proceed with the next experiment.

## V Acknowledgements

Professor James Heyman

*Physics and Astronomy Dept.*

*Macalester College*

Samples obtained from

Dr. Nelson Coates (Mac '03)

*Molecular Foundry, Lawrence*

*Berkeley National Laboratory*

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## VI Tables and Figures

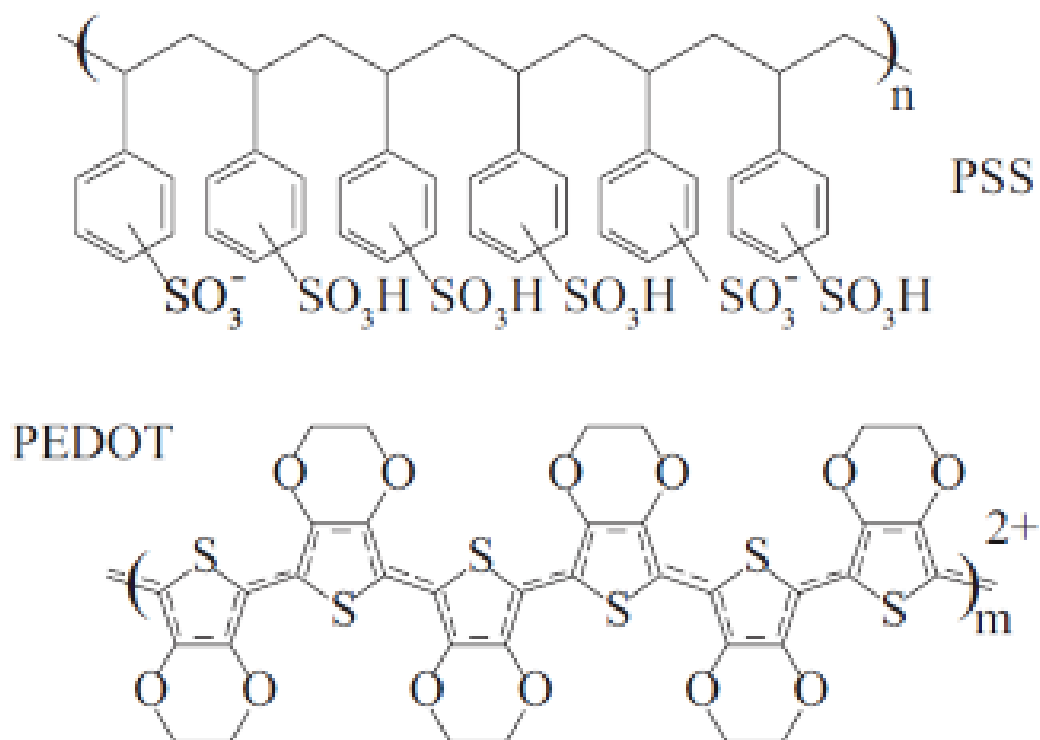


Figure 1: PEDOT:PSS chemical structure [2]

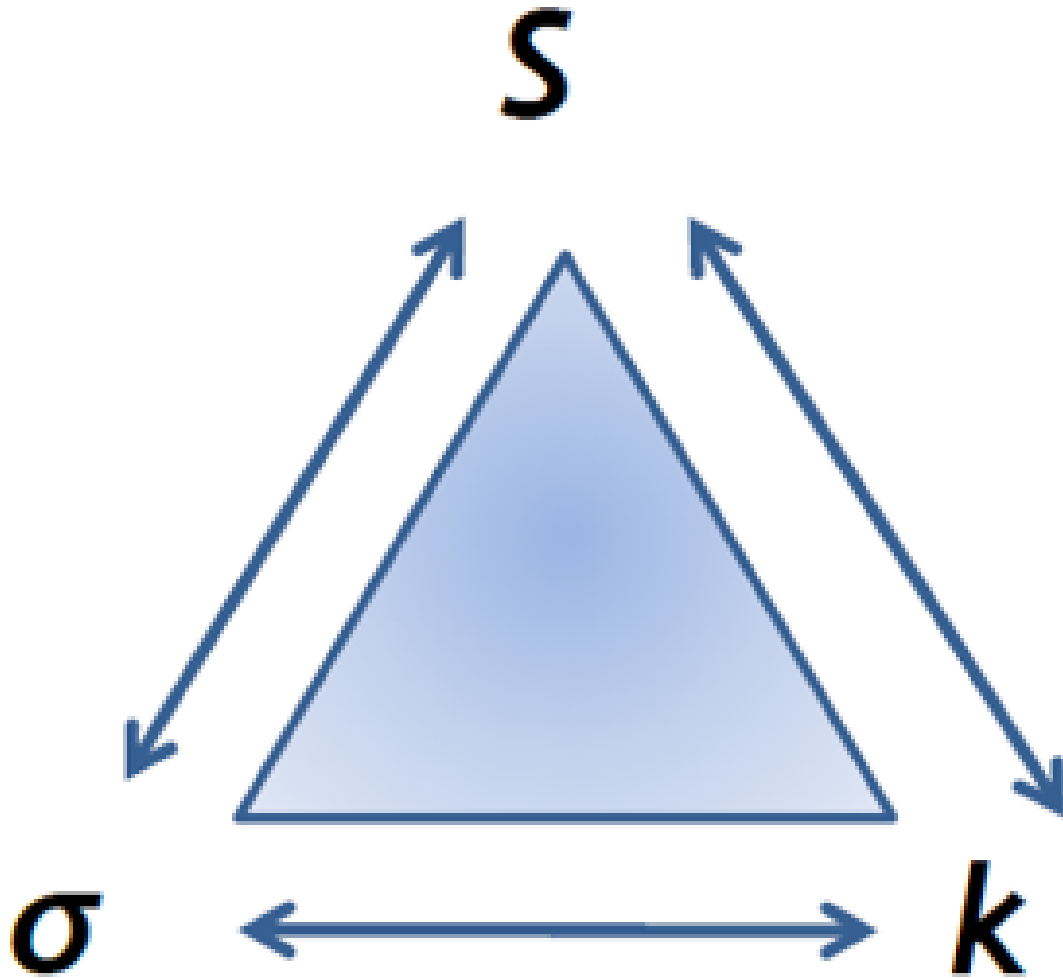


Figure 2: One of the primary challenge in developing advanced thermoelectric material is decoupling  $S, \sigma$  and  $k$ , which are typically strongly interdependent [3]

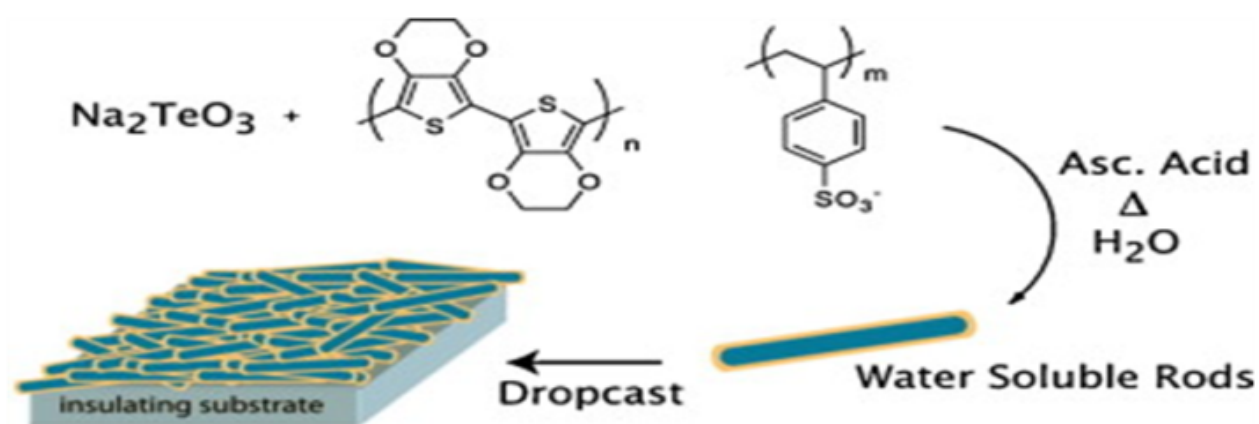


Figure 3: Tellurium nanowires on PEDOT:PSS. This material is solution-processable, which enables applications outside the bounds of traditional Tellurium manufacturing [2]

$N_{sample} > 20$	$\sigma$	$S$	$S^2\sigma$	$\kappa$
	(S/cm)	( $\mu$ V/K)	( $\mu$ W/m-K <sup>2</sup> )	(W/m-K)
	In-Plane	In-Plane	In-Plane	Through-Plane
<b>Hybrid</b>	19.3 ( $\pm$ 2.3)	163 ( $\pm$ 4)	70.9	0.10-0.30
<b>PEDOT:PSS</b>	1.32 ( $\pm$ 0.12)	18.9 ( $\pm$ 0.2)	0.05	0.24-0.29
<b>Te NWs</b>	0.08 ( $\pm$ 0.03)	408( $\pm$ 69)	2.7	2

Figure 4: The electrical conductivity of the hybrid material is much greater than the individual components [3]

Sample		Degrees			Radians (FWHM)			particle size(Å) using Scherrer Formula		
		[100]	[101]	[110]	[100]	[101]	[110]	[100]	[101]	[110]
	2θ	<b>23.08</b>	<b>27.68</b>	<b>40.08</b>	<b>23.08</b>	<b>27.68</b>	<b>40.08</b>	<b>23.08</b>	<b>27.68</b>	<b>40.08</b>
TeNW 1	FWHM	0.117	0.167	0.167	0.002042	0.002915	0.002915	1531.4	600.2	686.5
TeNW 2	FWHM	0.218	0.184	0.167	0.003805	0.003211	0.002915	821.9	544.8	686.5
TeNW 3	FWHM	0.200	0.167	0.184	0.003491	0.002915	0.003211	895.9	600.2	623.1
TeNW_PEDOT 2	FWHM	0.535	0.468	0.602	0.009338	0.008168	0.01051	334.9	214.2	190.4
TeNW_PEDOT 3	FWHM	0.335	0.402	0.602	0.005847	0.007016	0.010507	534.9	249.3	190.5
TeNW_PEDOT 4	FWHM	0.535	0.535	0.602	0.009338	0.009338	0.010507	334.9	187.4	190.5

Table 1: Te particle size calculated using Scherrer formula

XDR					SEM(EDAX)			
		Relative Concentration of [Te]			Samle/Si		Standardize (using first sample)	
Sample		[100]	[101]	[110]	L-series	M-series	L-series	M-series
	<b>2θ</b>	23.08	27.68	40.08	[Te]	[Te]	[Te]	[Te]
TeNW1		1	1	1	3.432692	0.030428	1	1
TeNW2		1.474909091	0.794073	0.911616	3.667379	0.02631	1.068368	0.864656
TeNW3		1.36969697	0.809271	1.093434	-	-	-	-
TeNW_PEDOT2		2.454545455	0.06307	1.704545	1.073332	0.001365	0.312679	0.044865
TeNW_PEDOT3		1.709090909	0.058511	1.772727	1.017968	-0.0009	0.296551	-0.02969
TeNW_PEDOT4		0.96969697	0.035714	0.856061	0.918455	-0.00197	0.267561	-0.06475

Table 2: Relative concentration of Te nanowires

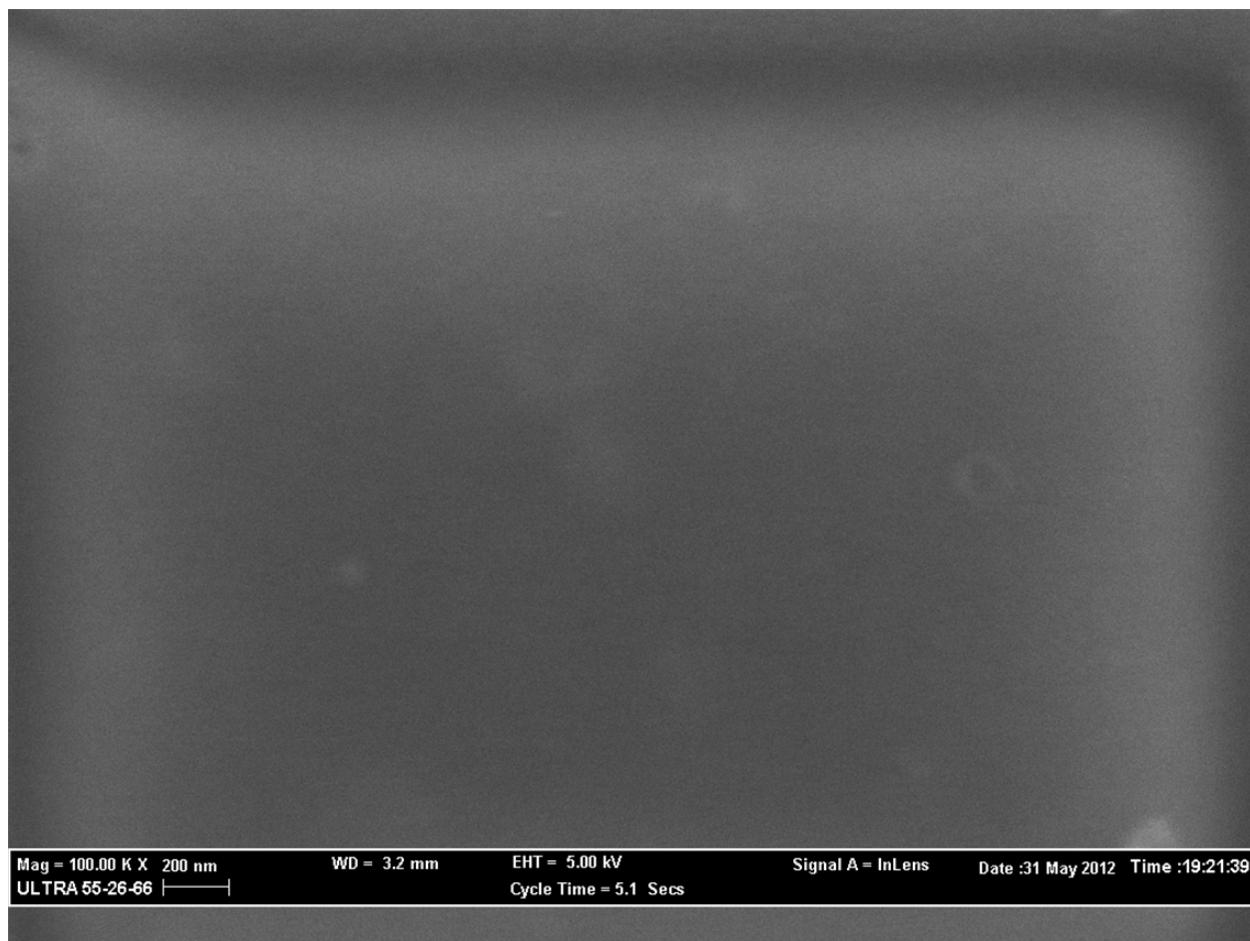


Figure 5: Pure PEDOT:PSS polymer film,  $100k\times$  magnification ( $200nm$  scale bar)

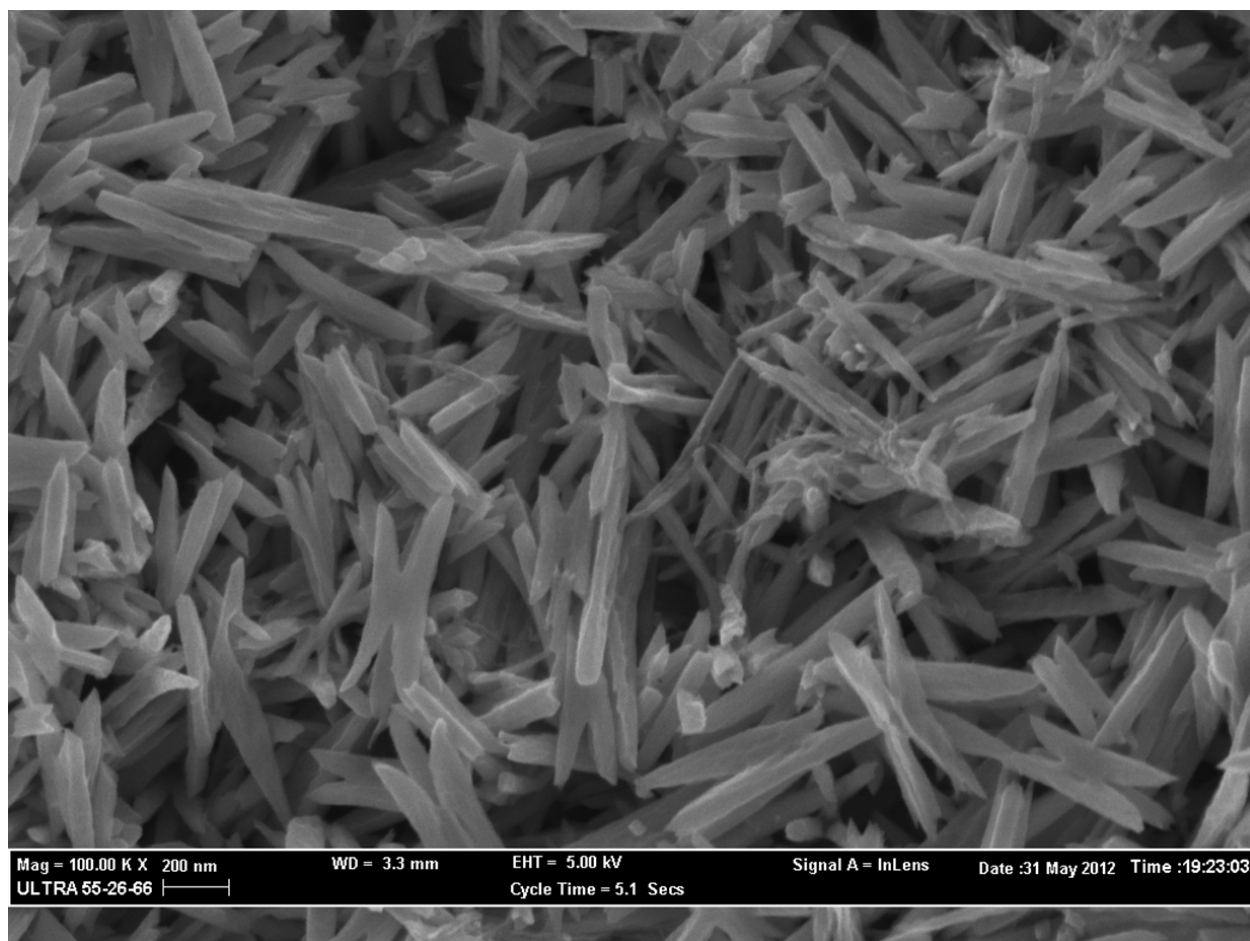


Figure 6: Pure Tellurium nanowire film, 100kx magnification (200nm scale bar)

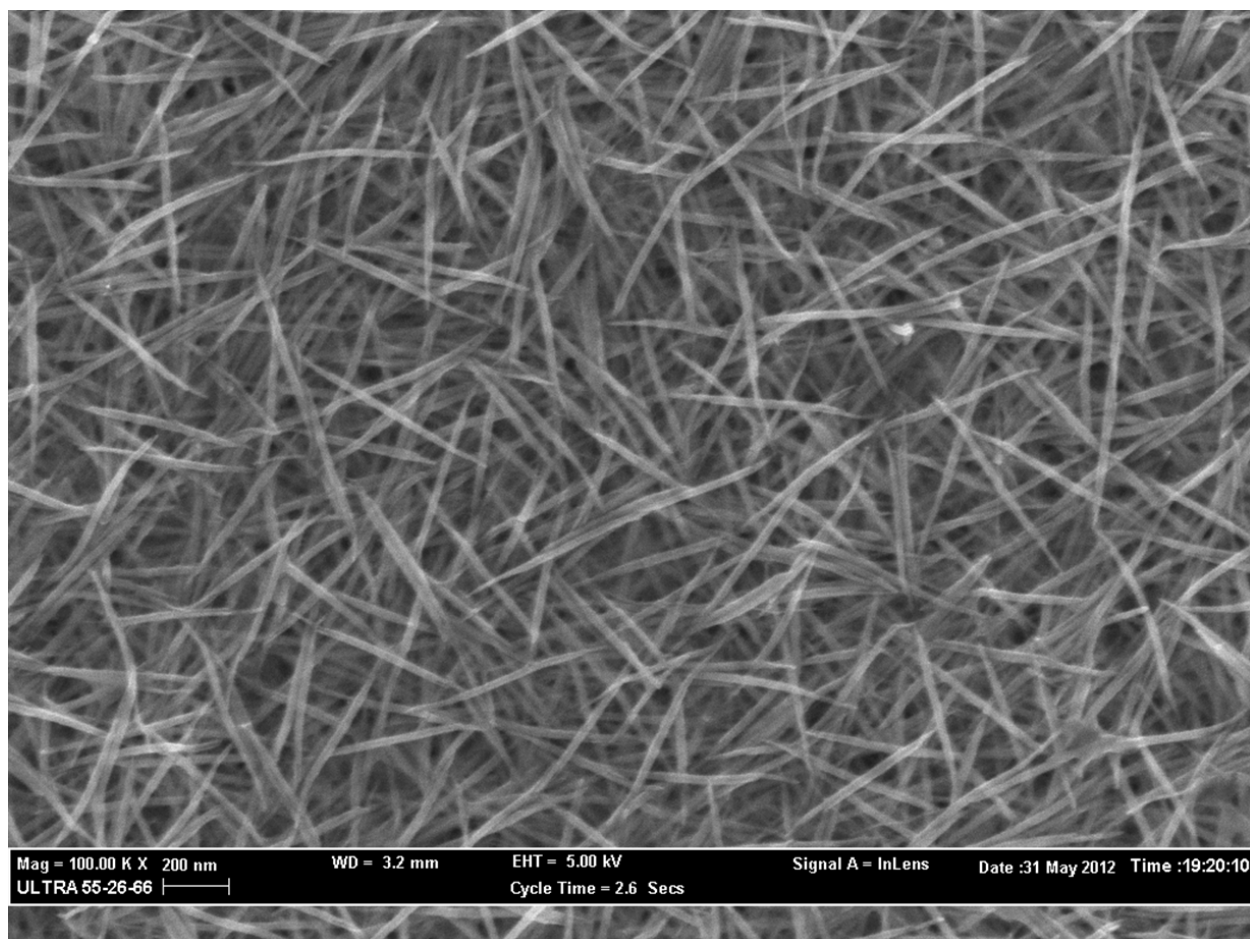


Figure 7: Co-synthesized Tellurium nanowire coated in PEDOT:PSS polymer, 100kx magnification (200nm scale bar)

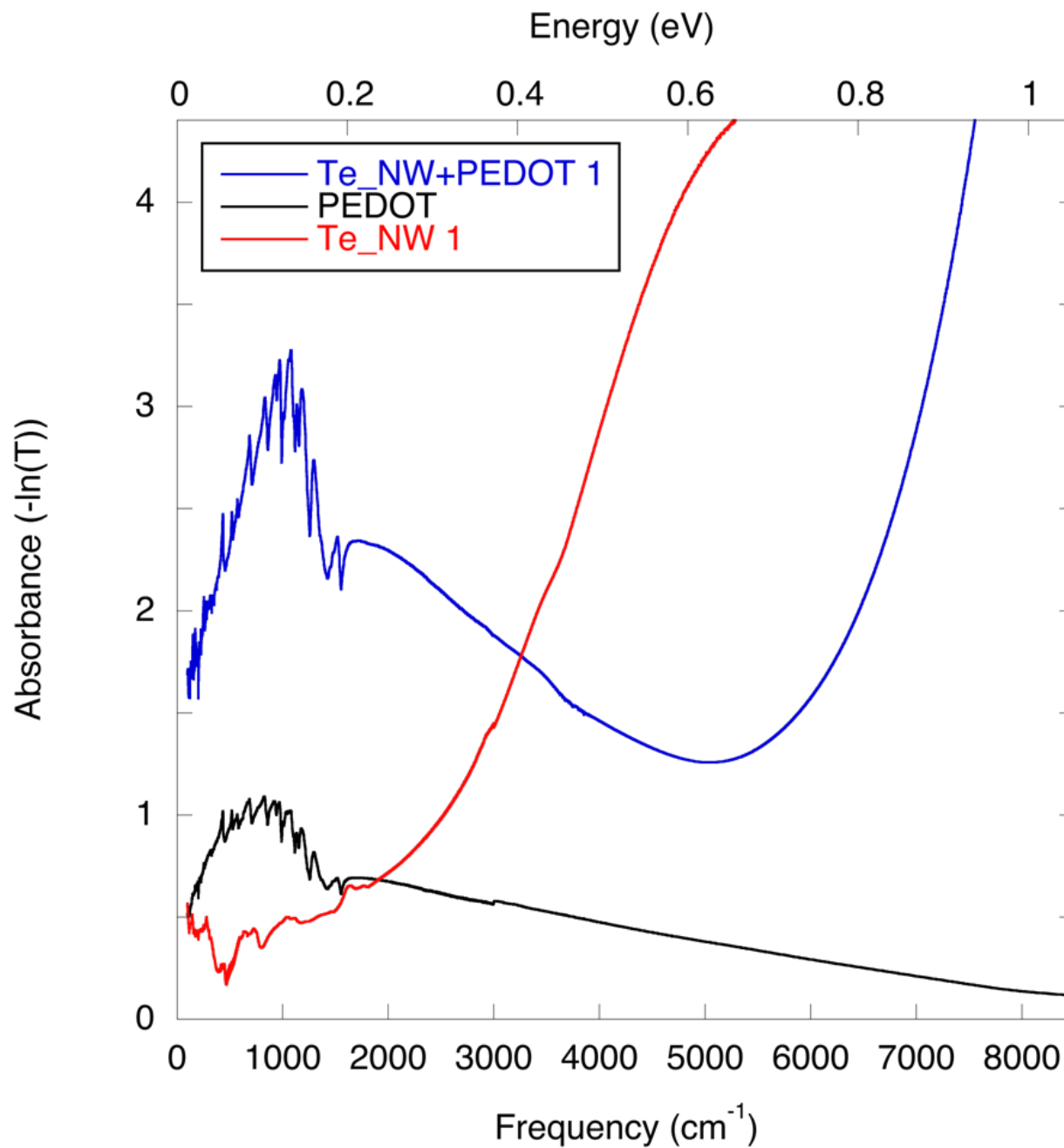


Figure 8: IR absorption for Te nanowire, PEDOT:PSS and Te + PEDOT:PSS (Te coated in PEDOT:PSS) samples

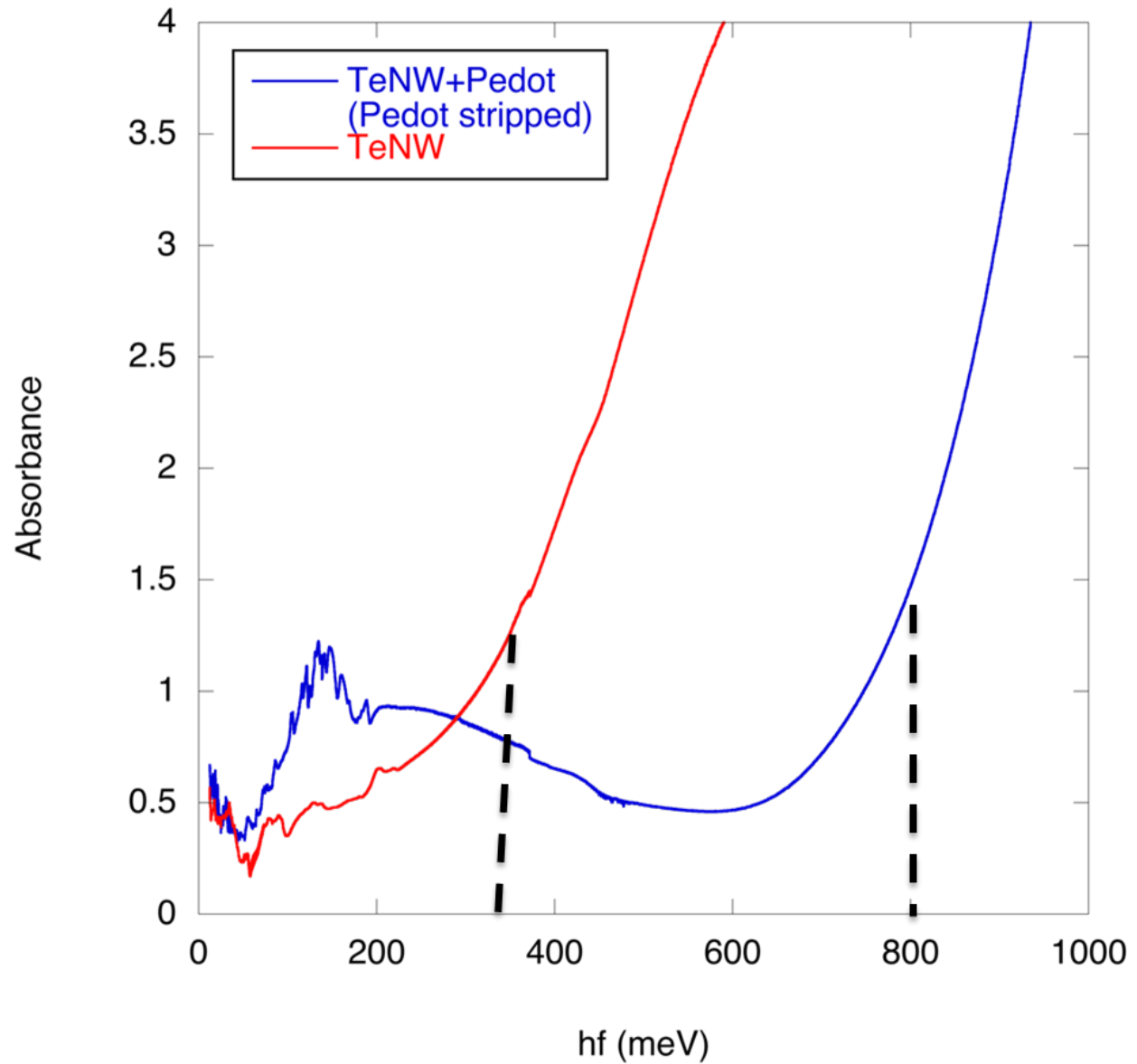


Figure 9: IR absorption in Te nanowire and Te+PEDOT:PSS with PEDOT features subtracted

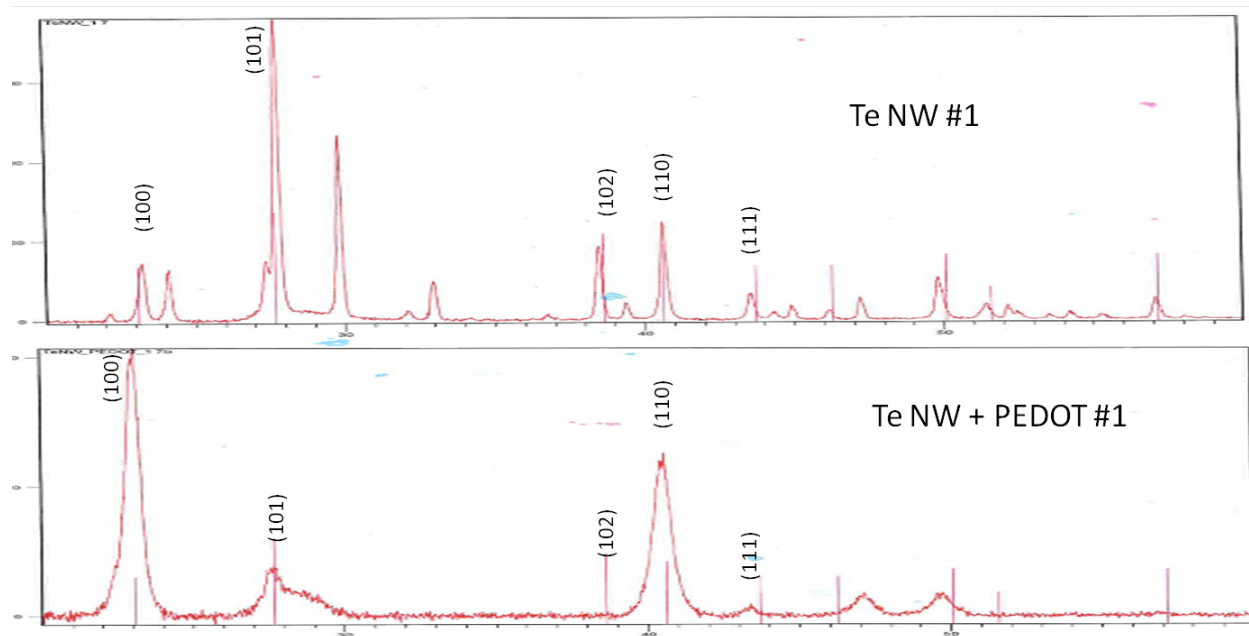


Figure 10: X-ray diffraction data for Te nanowires and Te+PEDOT:PSS samples. Vertical lines : predicted diffraction peaks for hexagonal Te (ordinary phase)

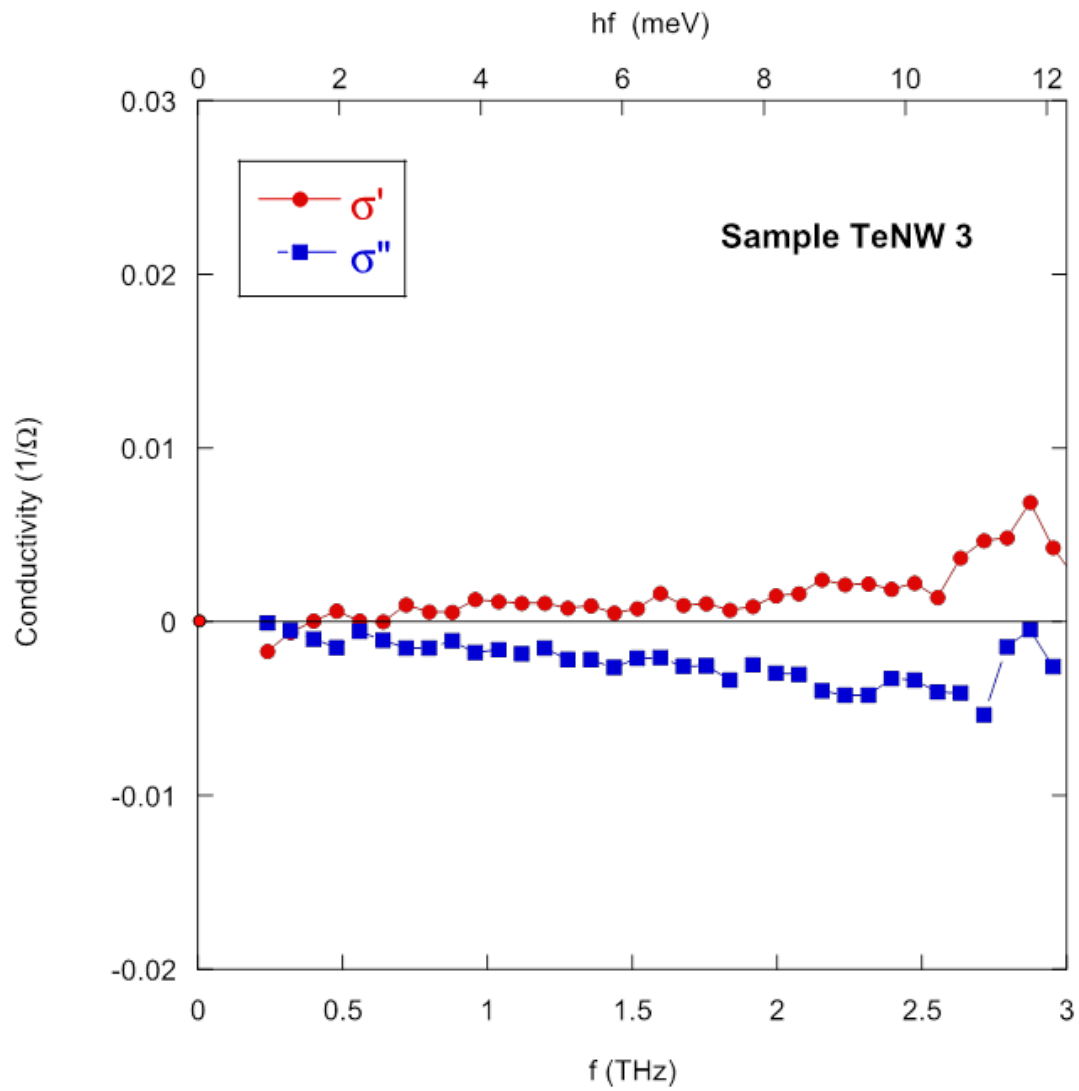


Figure 11: THz conductivity measurement of Te nanowires

## Conductivity vs. Frequency for pure Te NW and Te NW/PEDOT Samples

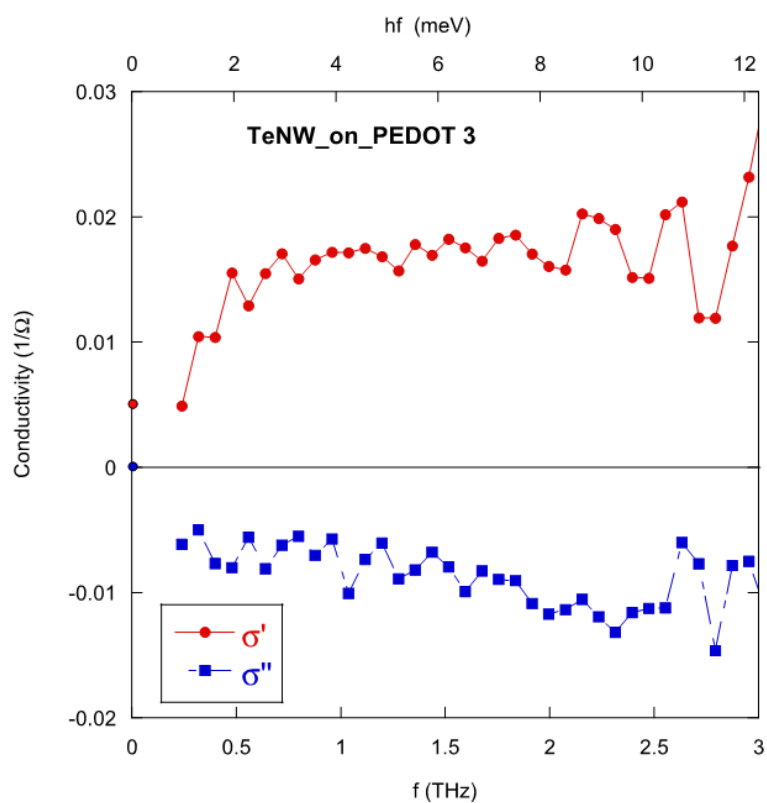


Figure 12: THz conductivity measurement of Te nanowires + PEDOT:PSS

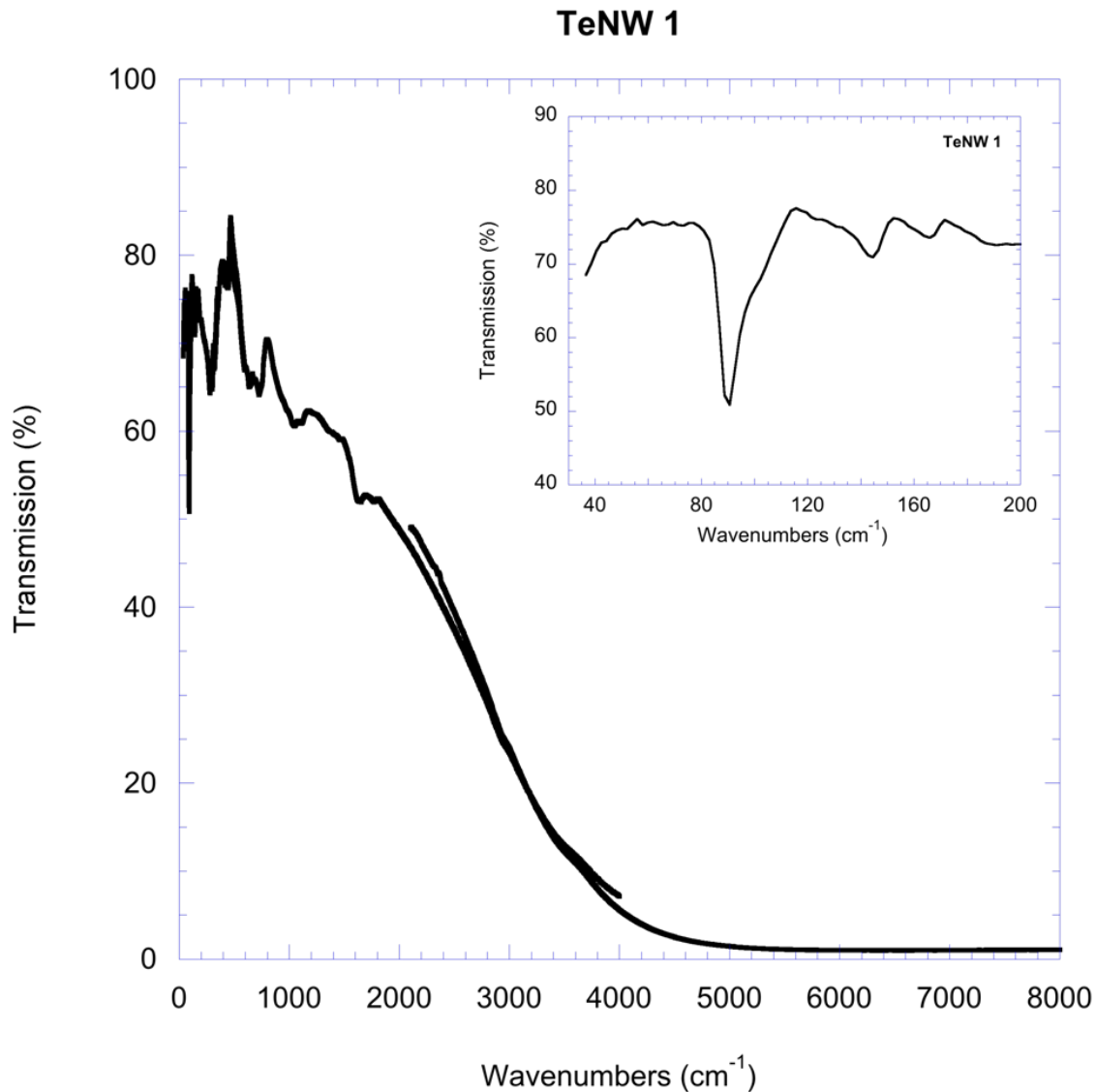


Figure 13: When we zoom in around  $100\text{cm}^{-1}$ , the far-infrared spectra containing Te show phonon absorption lines

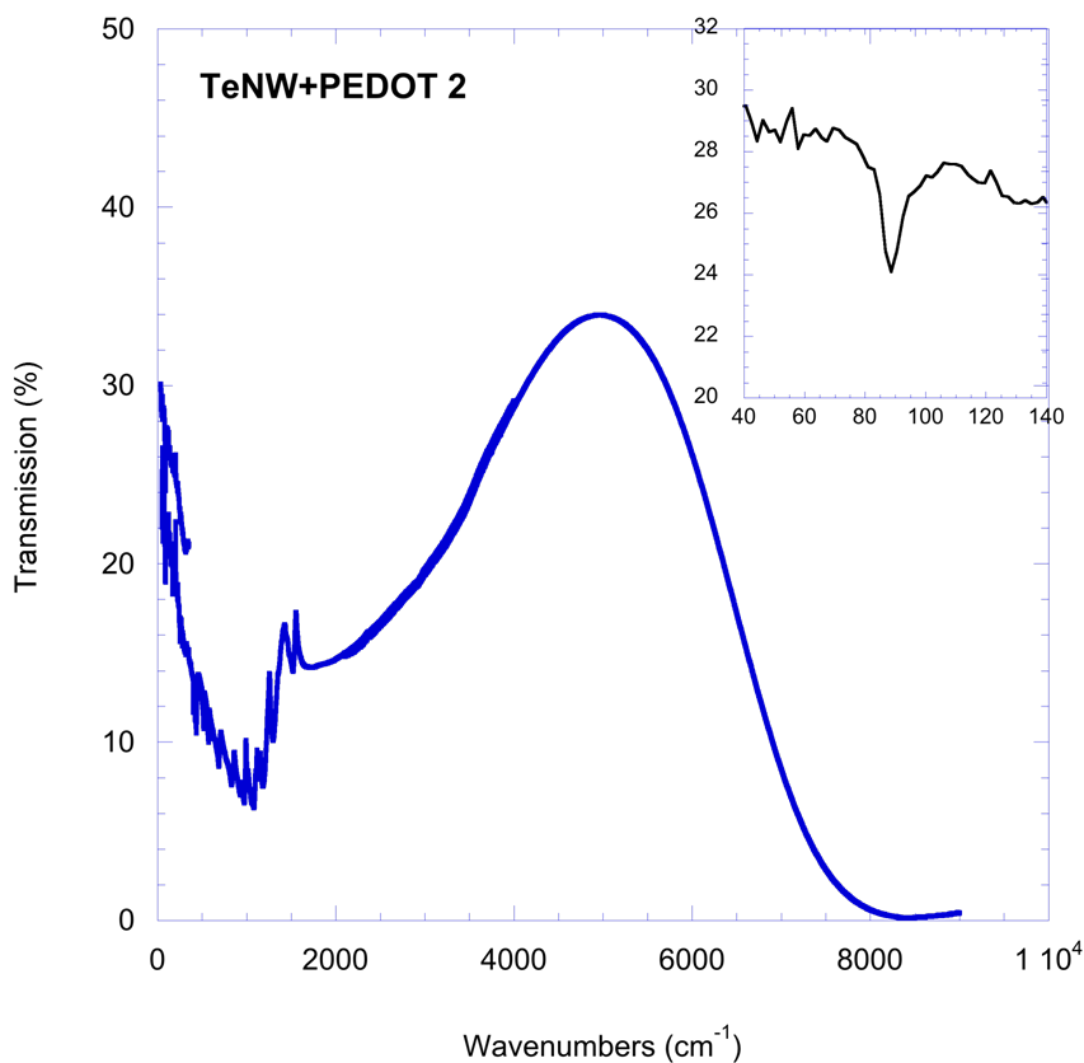


Figure 14: The same Te phonon absorption line is also seen in the Te+PEDOT:PSS

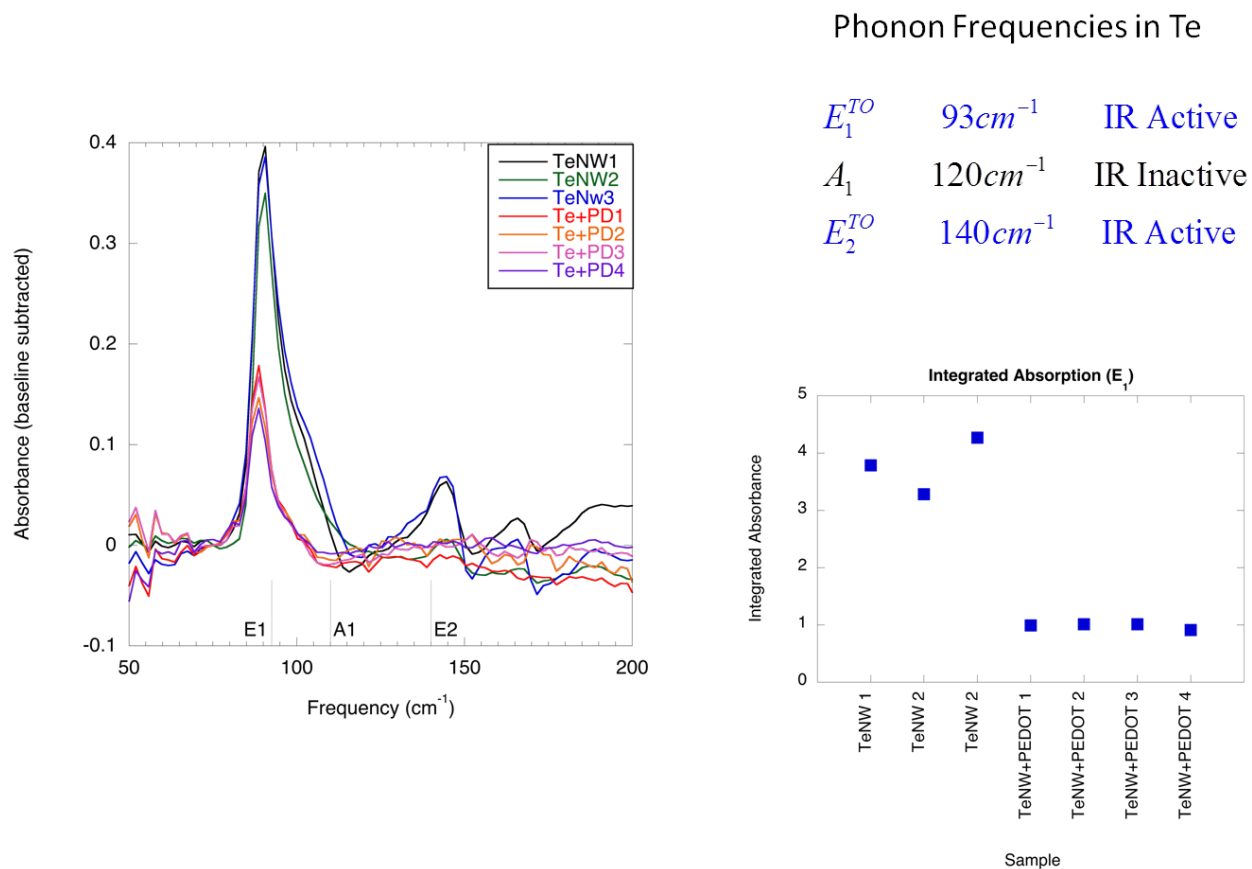


Figure 15: Far-infrared spectra show infrared allowed phonon modes in Tellurium. The pure Te samples show strong absorption compare to Te+PEDOT:PSS

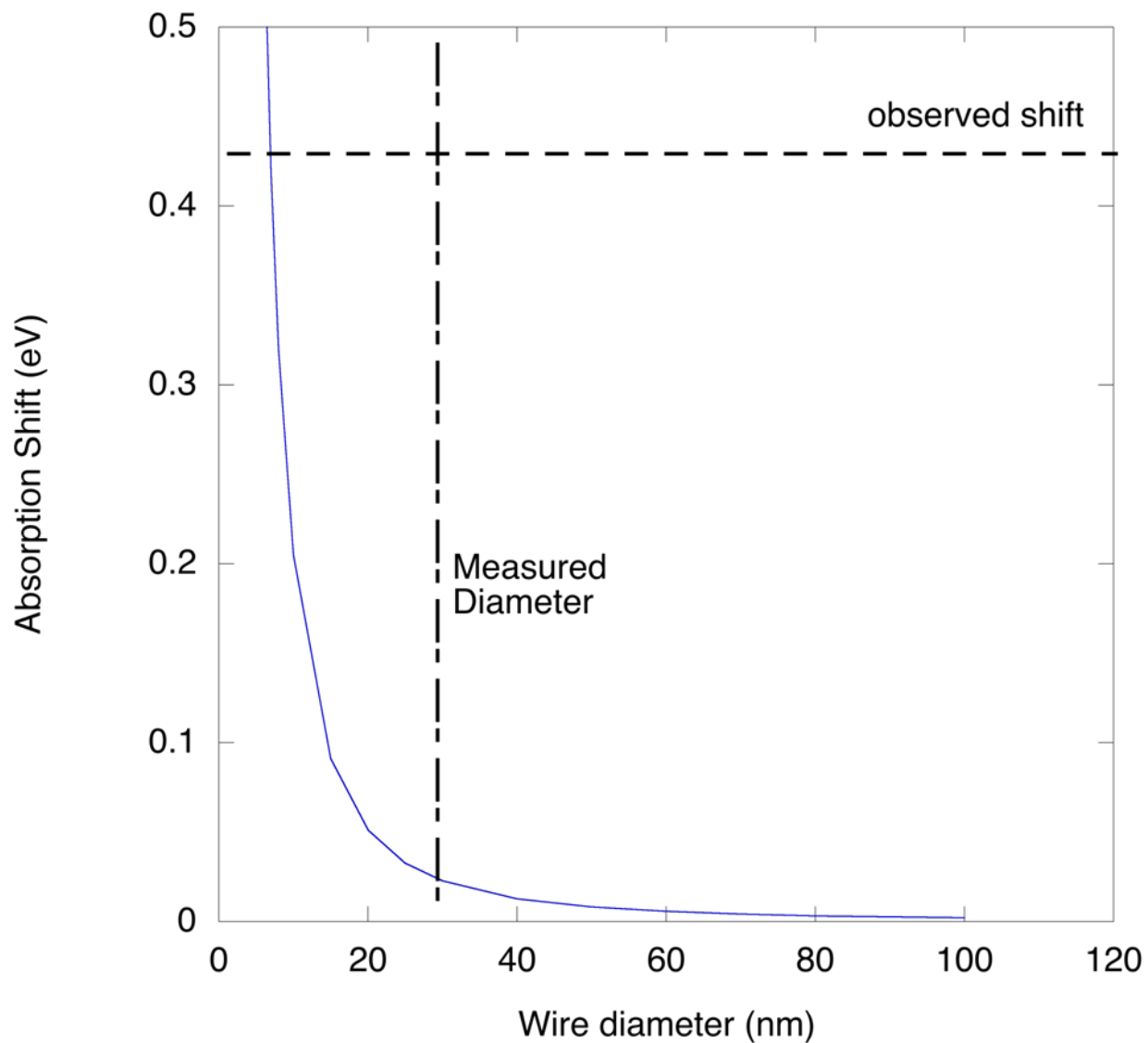


Figure 16: Confinement energy does not seem to explain the observed shift in absorption edge seen in Figure 10