

# Synthesis and thermoelectric properties of Tellurium Nanotube

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**Abstract:** Single crystalline tellurium nanotubes were synthesized using EG and TeO<sub>2</sub> as a source. FESEM analysis revealed a tube-like structure with spherical amorphous TeO<sub>2</sub> nanoparticles. Prepared nanotubes are unstable after prolonged storage, but can be stored in ethanol for three months without noticeable morphology changes. Tellurium nanotubes can be used as templates for tubular telluride or other materials. Some nanotubes aggregate, causing wider appearances. FESEM images reveal wedgelike open ends and sloping cross sections, indicating a semiconductor with increased electrical conductivity with temperature. The room temperature ZT value is 0.001 and previously reported ZT is about 0.005. Due to non-uniform structure of tellurium nanotubes, the ZT results five times lower than previously reported value. Uniform size reduction will increase the thermoelectric performances of tellurium nanotube in future.

Keywords:

## 1. Introduction

In the present era, nanomaterials open up a new direction of research which influences science and engineering [1, 2]. The broad area of research makes nanotechnology and nanoscience growing up worldwide and in future the research opportunity of nanotechnology will give an evolutionary change in mass market. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It has significant commercial impact, which will assuredly increase in the future. TE materials are those materials where mutual conversion between thermal to electrical energy is achieved based on

Seebeck-Peltier effect. These materials are characterized by the transport properties like electrical conductivity ( $\sigma$ ) thermal conductivity ( $\kappa$ ) and thermoelectric power ( $S$ ) to link with thermoelectric figure of merit ( $ZT$ ) defined as

$$ZT = S^2 \sigma T / \kappa = PT / \kappa \quad (1)$$

Where  $P = S^2 \sigma$  is the power factor.

In a 3D crystalline material  $\sigma$ ,  $S$  and  $\kappa$  are interrelated in such a way that it is very difficult to tune them independently. This is because increase in  $S$  results in decrease in  $\sigma$  and decrease in  $\sigma$  decreases the electronic contribution to  $\kappa$  according to Wiedemann-Franz law [3].

Tellurium is primarily used as an alloying agent. Small amounts of tellurium are added to copper and stainless steel to make them easier to machine and mill [4, 5]. Tellurium is also added to lead to increase its strength and resistance to sulfuric acid ( $H_2SO_4$ ). Tellurium is also used to color glass. Tellurium forms many compounds. They include: tellurous acid ( $H_2TeO_2$ ), tellurium tetrachloride ( $TeCl_4$ ), tellurium dichloride ( $TeCl_2$ ), tellurium trioxide ( $TeO_3$ ), tellurium monoxide ( $TeO$ ) and sodium telluride ( $Na_2Te$ ).

Recently, synthesis of semiconducting crystals with well-defined morphologies, such as wires, rods, belts, tubes, spheres, and flowers has attracted significant attention because of their unique properties and applications in electronics and photonics devices. For example, one-dimensional (1D) nanostructures [nanorods (NRs), nanowires (NWs), and nanotubes (NTs)] [6] are of particular interest because of their unique structures and potential applications in fundamental research and industry. Among these 1D nanostructured materials, trigonal tellurium (Te) is an interesting one and tends to form 1D structures with or without templates and surfactants. Trigonal Te has a highly anisotropic crystal structure consisting of helical chains of covalently bound atoms, which are

bound together through van der Waals interactions in a hexagonal lattice; therefore, resulting in consistent growth of crystals along the c-axis, which have a pronounced tendency to form 1D nanostructures. In addition, trigonal Te with a narrow direct bandgap (0.35 eV) [7] exhibits many interesting properties such as photoconductivity, thermoelectricity, piezoelectricity, catalytic activity, and nonlinear optical properties. These unique properties of 1D Te nanostructures result in many potential applications such as gas sensors, electronic and optoelectronic devices, self-developing holographic recording devices, radiative cooling devices. So, it is convenient to synthesis the nanostructures of Te.

Synthesis of self-aligned tellurium nanotubes by Sodium thiosulfate have done [8]. 0.3 g of PVP and 0.1 g of  $\text{Na}_2\text{S}_2\text{O}_3$  were added to a 50 ml round-bottom flask containing 30 ml EG and the mixture was then heated to  $100^\circ\text{C}$  under nitrogen flow and vigorous stirring. 0.11 g (0.5 mmol) of  $\text{Na}_2\text{TeO}_3$  was added to solvent and maintained at  $180^\circ\text{C}$  for 1h. After the mixture was cooled down to room temperature, the obtained product was filtered and washed with distilled water and absolute ethanol and dried at  $100^\circ\text{C}$  for 5 h. During Te nanotube synthesis, EG served as both a solvent and a reducing agent. The individual tellurium nanotubes exhibited well-aligned morphologies with diameters of 150-250 nm, lengths of 5-8  $\mu\text{m}$  and wall thicknesses of 70-80 nm. The nanotubes preferentially self-aligned along the c-axis direction and gradually formed well-aligned nanotubes with hexagonal prism structures. The presence of  $\text{Na}_2\text{S}_2\text{O}_3$  plays a crucial role in controlling self-alignment of nanostructures, as well as varying their dimensional structure. If no  $\text{Na}_2\text{S}_2\text{O}_3$  was added, and the other conditions remained unchanged, the products consisted mainly of un-aligned nanotubes. The outer layers of the Te nanotubes tend to be easily oxidized in air. It has been concluded that because the atoms at the surface are more active than the inner atoms, nanotubes are more easily oxidized in air. Controlled synthesis of crystalline tellurium

nanorods, nanowires nanobelts have prepared related by solution process [9]. Single crystalline nanotubes and nanowires of t-Te have been prepared by a simple solution route. The procedure involves of NaHTe, prepared by the reduction of Te with NaBH<sub>4</sub>. By carefully controlling the reaction conditions, the diameter of the nanorods could be varied in the 20–300 nm range. Nanowires of 10 nm diameter were obtained in the presence of sodium dodecylbenzenesulfonate (NaDBS). Synthesis in aqueous medium [9], 0.0300 g (0.234 mmol) of Te was taken in 20 ml of deionized water in a 250 ml round bottom flask fitted to a nitrogen cylinder. The flask was purged with nitrogen thoroughly. This was heated to 90-degree C. 0.0500 g (1.3 mmol) of NaBH<sub>4</sub> was added to the flask and the reaction mixture was again purged with nitrogen. The solution turned black immediately. The solution turned pink and after a period of 30 minutes, all the Te dissolved. The solution was diluted, as required, with deionized water heated to the reaction temperature and then the reaction solution was brought to room temperature by natural cooling. The solution slowly turns blue. The product which settled down at the bottom of the reaction vessel was washed several times with deionized water and air-dried before further characterization. This product generally contained nanorods. Te nanowires could be obtained when the above procedure was carried out in the presence of sodium dodecylbenzene sulfonate (NaDBS). Synthesis in a non-aqueous medium, Te nanorods was carried out at 150<sup>0</sup> C under conditions in ethylene glycol or diethylene glycol for two hours. The quantities of the reactants were the same as in the aqueous synthesis. The reaction mixture was cooled to room temperature after refluxing for 2 hours and the resulting solution was kept as such for one week. The X-ray photoelectron spectrum of the nanorods gave two peaks at 573.6 and 583.8 eV corresponding to the Te 3d<sub>5/2</sub> and 3d<sub>3/2</sub> states respectively.

Hydrothermal preparation of tellurium nanotubes in presence of formamide and growth mechanism observed. 0.0005 mol of sodium tellurate ( $\text{Na}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ ), 25 mL of NaOH (1 M), and 30 mL of formamide ( $\text{HCONH}_2$ ) were added into a Teflon-lined stainless-steel autoclave of 60 mL capacity, which gave final concentrations of 0.0091 mol  $\text{TeO}_4$ , 0.45 mol, and 3.66 mol  $\text{HCONH}_2$ . The autoclave was sealed and maintained at 160 °C for 20 h. After that, the autoclave was allowed to cool to room temperature naturally. It was found that a large quantity of dark gray particles floated on the top of the solution. The dark gray particles were filtered off and washed several times with distilled water and absolute ethanol to remove impurities and then dried in a vacuum at 50 °C for 4 h.

In this work, with EG (ethylene glycol) as a reductant and Tellurium dioxide ( $\text{TeO}_2$ ) as the tellurium source, single crystalline tellurium nanotubes were successfully synthesized in the presence of cetyltrimethylammonium bromide (CTAB).

## **2. Experimental**

### ***2.1. Material Used:***

Tellurium dioxide ( $\text{TeO}_2$ ) is used as the tellurium source and EG used as both reductant and solvent in the presence of cetyltrimethylammonium bromide (CTAB). Distilled water and ethanol used to wash the sample Tellurium dioxide ( $\text{TeO}_2$ ) was purchased from Alfa Aesar. Ethanol was purchased from Merck chemicals. All the chemicals received, were of analytical grade and used without further purification.

### **2.2. Synthesis Of Tellurium Nanotube:**

In a typical procedure for the synthesis of tellurium nanotubes,  $\text{TeO}_2$  (0.4 g) and CTAB (cetyltrimethylammonium bromide) (0.92 g) were added to a 100-mL Teflon-lined stainless-steel autoclave. Then the autoclave was filled with EG (ethylene glycol) up to 80% (80ml) of the total

volume, and the reaction mixture formed a homogeneous white suspension under vigorous stirring. The autoclave was sealed and maintained at 180 °C for 24 h, then cooled to room temperature naturally. The final silver-gray product was collected by centrifugation the reaction mixture, and then the particle washed with distilled water and absolute ethanol several times each and, dried in a vacuum at 60 °C for 6 h.

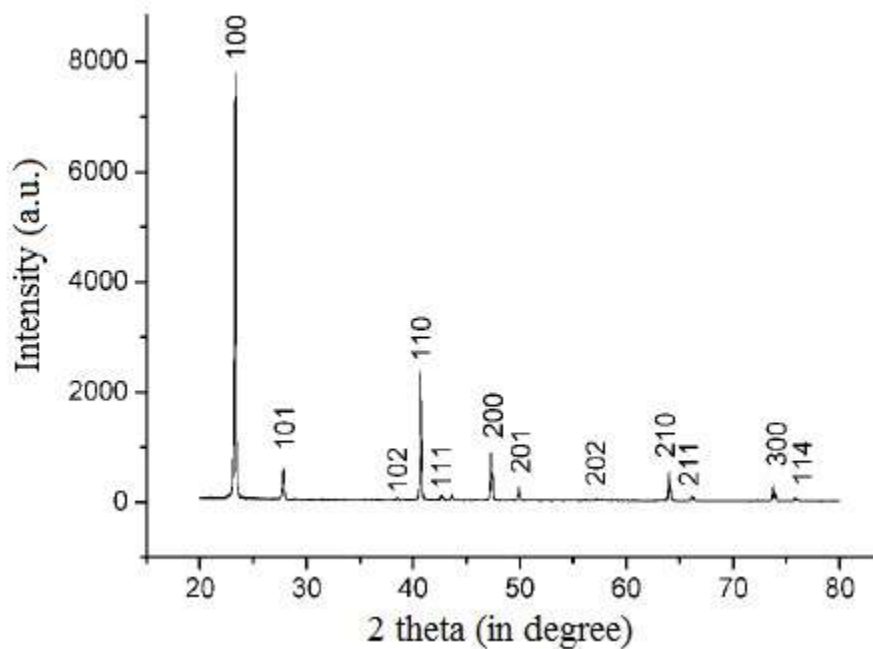
### **3. Characterization**

The phase purity of the as-prepared products was examined by X-ray diffraction (XRD) using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu KR radiation ( $\lambda$  1.54178 Å). The synthesized sample was structurally characterized by field emission scanning electron microscope (FESEM) to investigate the size and morphology and was carried out with a field-emission scanning electron microanalyzer (JEOL-6700F).

The prepared sample was pressed at room temperature under 2 tons pressure and cut into small rectangular pieces for measurement of the electrical transport properties. The variation of the electrical conductivity ( $\sigma$ ) as well as thermoelectric power (S) with temperature were carried out in the range 290-400 K for the sample. The electrical conductivities of the sample were measured by four probe method using a four probe setup (Model No DFP 301). For the measurement of thermoelectric power, an auxiliary heater was placed at one end of the sample holder to establish a temperature difference, while the corresponding potential drop was measured by a Hewlett Packed data acquisition system (Model no 34970A). Room temperature thermal conductivity was collected from literature.

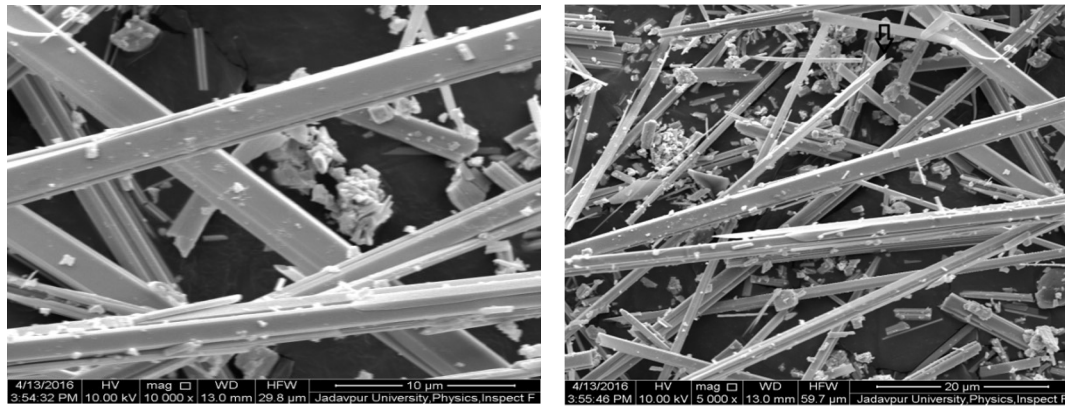
#### 4. Result and discussion

The X-ray diffraction (XRD) pattern shown in Figure 1 that all diffraction peaks can be indexed as hexagonal phase of tellurium with lattice constants  $a = 0.446$  nm and  $c = 0.591$  nm, which are in agreement with the reported values (JCPDS, 36–1452). No other impurity was detected by the X-ray diffraction pattern. Compared with the standard pattern of hexagonal phase tellurium, unusually strong ( $h00$ ) reflection peaks and weak ( $hkl$ ) reflection peaks ( $l \neq 0$ ) were observed in the XRD pattern.



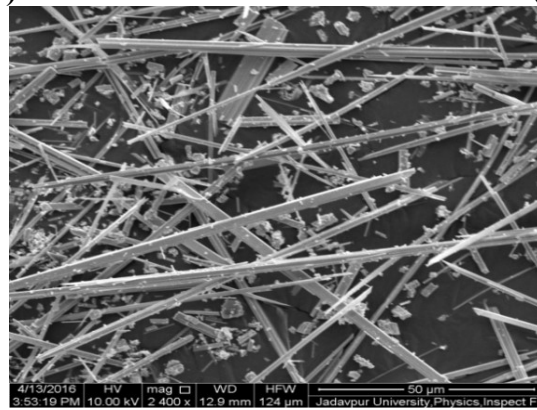
**Figure 1. XRD pattern of the as-prepared tellurium nanotubes**

The sample was measured by a field emission scanning electron microscope (FESEM) at an acceleration voltage of 10 kV. Figure 1 shows the FESEM image of Tellurium nanotube. It is observed from the FESEM image that many particles of Tellurium dioxide are attached on the outer wall of Te nanotube. It is because the sample becomes oxidize when it is kept under air and water.

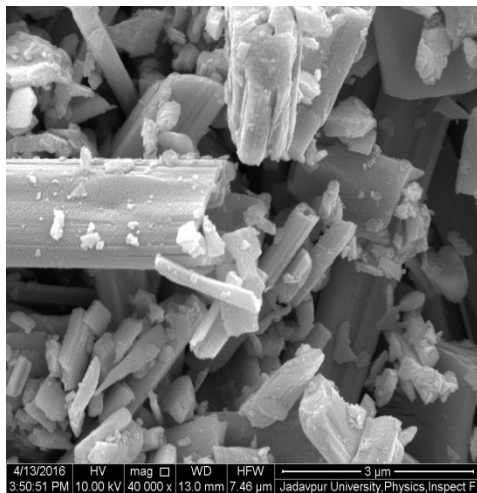


(a)

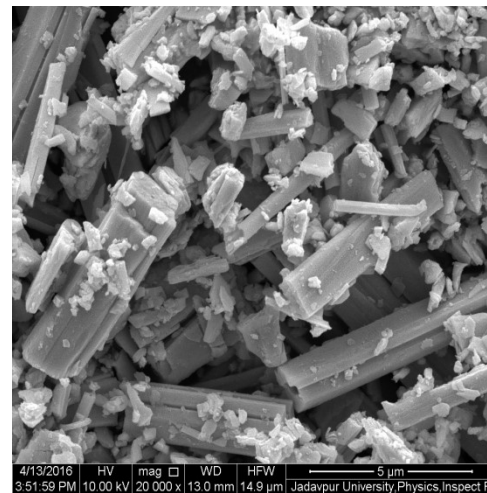
(b)



(c)



(d)



(e)

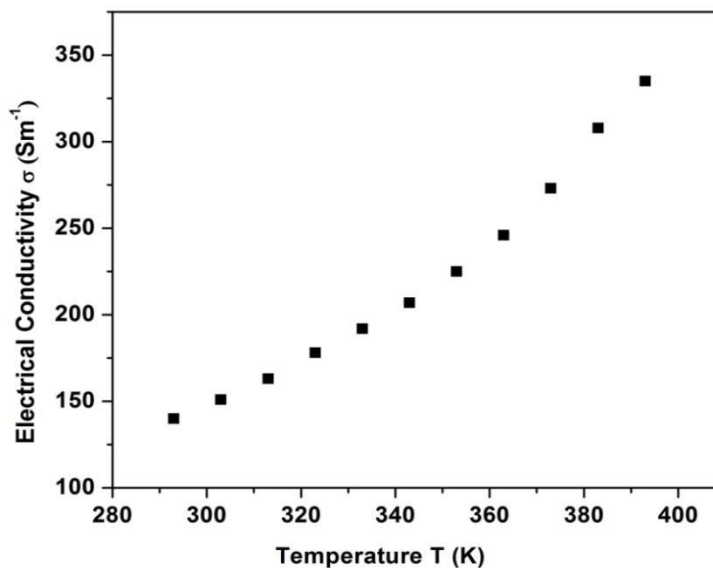
**Figure 2 (a,b,c,d,e) FESEM image of Tellurium nanotube**



Figure 2. (a) (b) (c) (d) and (e) are high magnification image which shows many Tellurium Oxide particles attached on the outer wall. we can see tube like structure (a,b,c) clearly and the tubes are genuinely hollow (d,e). Outer diameters varies from 200 nm to 4.6  $\mu\text{m}$  and wall thicknesses varies from 50 nm to 200 nm which have clearly observed from FESEM images (images a,b and c in Figure 2).

FESEM image at high magnification indicated that some of the nanotubes aggregated into bundles in the solution or during the preparation of SEM sample. This explains why some of the nanotubes look wider than the others (in a,b,c). FESEM image at high magnification; As indicated by an arrow in (b) revealing the sloping cross sections for Te nanotubes and it shows wedgelike open ends.

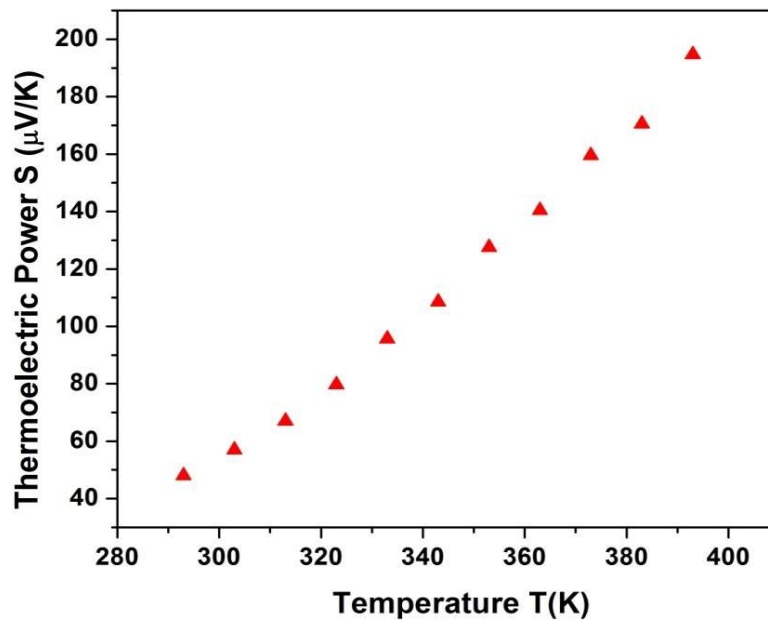
The temperature variation of the electrical conductivity ( $\sigma$ ) of the prepared sample is shown in figure 3. It is observed from the figure that for this sample the  $\sigma$  value that is electrical conductivity increases with a rise in temperature.



**Figure 3. Electrical conductivity of tellurium nanotube**

For the electrical conductivity of the Te nanotube the room temperature value was 140 S/m, which was calculated based on the 4-probe measurements. A typical 4-probe technique was used to measure the electrical conductivity. The increase in electrical conductivity with temperature suggests that the material is a semiconductor. High-efficiency thermoelectric materials require a high electrical conductivity. To measure thermoelectric performance, electrical conductivity plays a crucial role, low dimensions give an additional control and the quantum confinement effects arises, so we can easily increase electrical conductivity without decrease of thermoelectric power and can create high performance semiconducting materials.

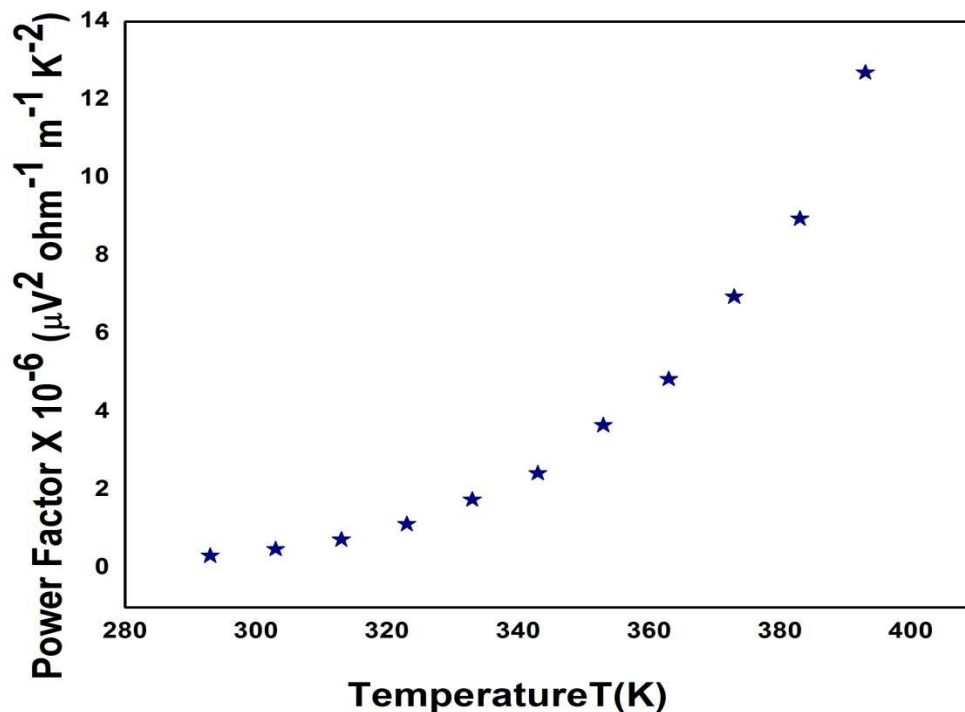
Figure 4 shows the variation of thermoelectric power (S) with temperature for the prepared sample. It is observed from the figure 4 that the thermoelectric power increases with the increase in temperature for the prepared sample. The positive S value of the sample indicates that the majority carriers are hole that is, it is a p-type semiconductor.



*Figure 4. Thermoelectric power of tellurium nanotube*

As suggested by Park [10] this increase in the value of  $S$  with temperature is an indication of diffusive metallic thermoelectric power. In room temperature thermoelectric power is  $48 \mu\text{V}/\text{K}$ . The thermoelectric power was measured by heating one pellet block and simultaneously measuring  $\Delta T$  and the thermoelectric voltage generated.

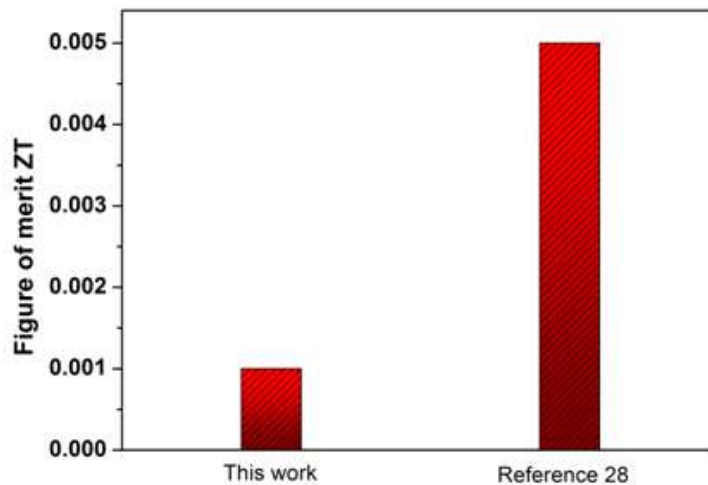
The electrical conductivity and thermoelectric power combine to yield the power factor given by  $S^2\sigma$ . The room temperature power factor is about  $0.322 \times 10^6 \mu\text{W}/\text{mK}^2$ . The temperature variation power factor of the prepared sample is shown in fig 5, it is observed that the power factor increases with increase in temperature.



*Figure 5. Power factor of tellurium nanotube*

The essential condition for enhancement of the figure of merit ( $ZT$ ) are the increase in the power factor ( $S^2\sigma$ ) as well as the decrease in the thermal conductivity. Theoretical value of thermal conductivity of Tellurium nanotube is  $1 \text{ W}/\mu\text{.K}$  [11].

The room temperature figure of merit has been evaluated from the electrical conductivity, thermoelectric power and thermal conductivity of the prepared sample. From calculation room temperature  $ZT$  value is 0.001. Previously reported  $ZT$  is about 0.005[12] for tellurium nanotubes. It is predicted that maximum  $ZT$  could reach 0.31 at room temperature for tellurium nanotube. Different devices have different ability to change temperature differences into thermovoltage. This ability is measured by the thermoelectric figure of merit  $ZT$ . It is used to characterize thermoelectric performance of a device.



***Figure 6. Figure of merit  $ZT$  of tellurium nanotube***

## 5. Conclusion

In summary, with EG (ethylene glycol) as a reductant and Tellurium dioxide ( $\text{TeO}_2$ ) as the tellurium source, single crystalline tellurium nanotubes were successfully synthesized in the presence of cetyltrimethylammonium bromide (CTAB). The FESEM investigation indicated clearly the tube-like structure and many spherical amorphous  $\text{TeO}_2$  nanoparticles were attached on the outer wall of Te nanotubes. The results demonstrate that the freshly prepared Te nanotubes are not stable after being stored for a prolonged time in contact with air and water. To prevent this situation, the nanotubes can be stored for three months in ethanol. There will be no obvious morphology changes between the freshly prepared sample and the sample after being stored for 3 months in ethanol. The prepared Tellurium nanotubes may be used as templates for the preparation of tubular telluride or other materials. Some of the nanotubes aggregated into bundles in the solution or during the preparation of SEM sample. This explains why some of the nanotubes look wider than the others. FESEM image shows wedgelike open ends and revealing the sloping cross sections for Te nanotubes. The increase in electrical conductivity with temperature suggests that the material is a semiconductor. The positive S value of the sample indicates that the majority carriers are hole that is, it is a p-type semiconductor. The room temperature ZT value is 0.001 and previously reported ZT is about 0.005. Due to non-uniform structure of tellurium nanotubes, the ZT results five times lower than previously reported value. Uniform size reduction will increase the thermoelectric performances of tellurium nanotube in future.

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