Hydrothermal Synthesis and Thermoelectric Transport Properties of Uniform Single-Crystalline Pearl-Necklace-Shaped PbTe Nanowires

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- ✓ One-dimensional (1D) nanomaterials are of great interest for the construction of high-performance thermoelectric devices.

- ✓ Thermoelectric materials have important applications in power energy generation, cooling, and thermal sensing.

$$ZT = \frac{TS^2\sigma}{k_e + k_L}$$

- ✓ **Seebeck coefficient** of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material.

- ✓ The calculations showed that the maximum *ZT* of 1D quantum wire is greater than that of both the bulk material and quantum well.

- ✓ There is no significant improvement in *ZT* value was reported and the template materials were suspected to cause complications for transport measurements.

- ✓ As prepared nanowires are usually polycrystalline.

- ✓ It is therefore essential to develop an alternative approach to prepare a large quantity of single crystalline thermoelectric nanowires to meet the demand of high-performance thermoelectric applications.

This Paper Presents……….

Lead telluride (PbTe) is a thermoelectric materials due to its narrow band gap (0.31 eV), *fcc* structure and large average excitonic Bohr radius (about 46 nm).

To improve the thermoelectric properties of PbTe remarkably, nanowires with diameter smaller than its average excitonic Bohr radius are highly desirable.

The performance of periodic or superlattice nanowires may outperform completely smooth nanowires because of the multiple scattering of acoustic phonons in periodic structured nanowires and increasing wire surface area

Hydrothermal synthesis method has been developed to synthesize single-crystalline pearlnecklace-shaped PbTe nanowires with the average external diameter of about 30 nm in large quantities.

Seebeck coefficient has enhanced 16% over the state-of-the-art bulk PbTe materials.

Experimental Protocol

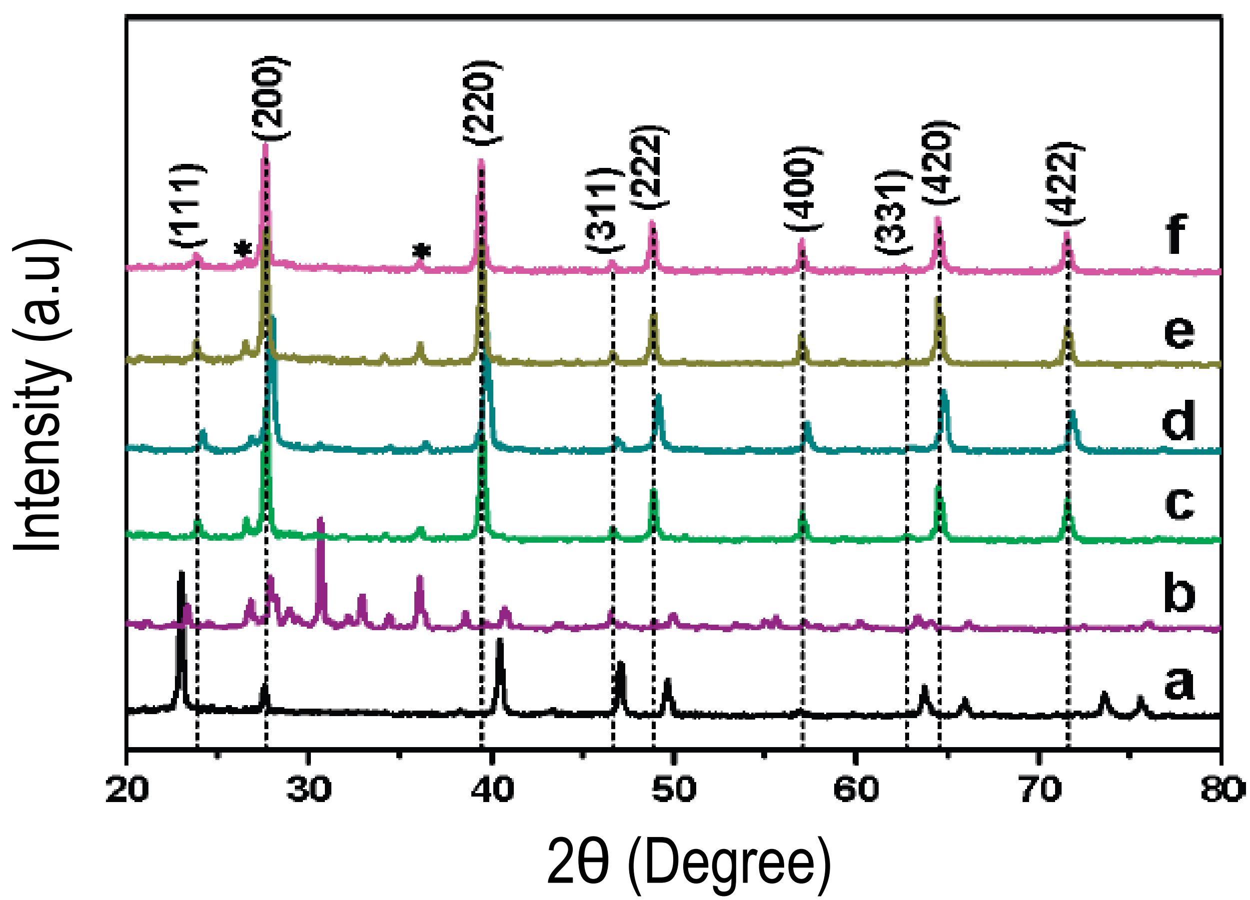
Synthetic Procedure for Tellurium Nanowires

0.30 g of polyvinyl pyrrolidone, K30
+ 0.1808 g of Na_2TeO_3 (0.8 mmol)
+ 25 mL of double distilled water $\xrightarrow{\text{453 K / 24 hrs.}}$ Te Nanowire
+ 1.5 mL of hydrazine hydrate
+ 3 mL of aqueous ammonia (25%)

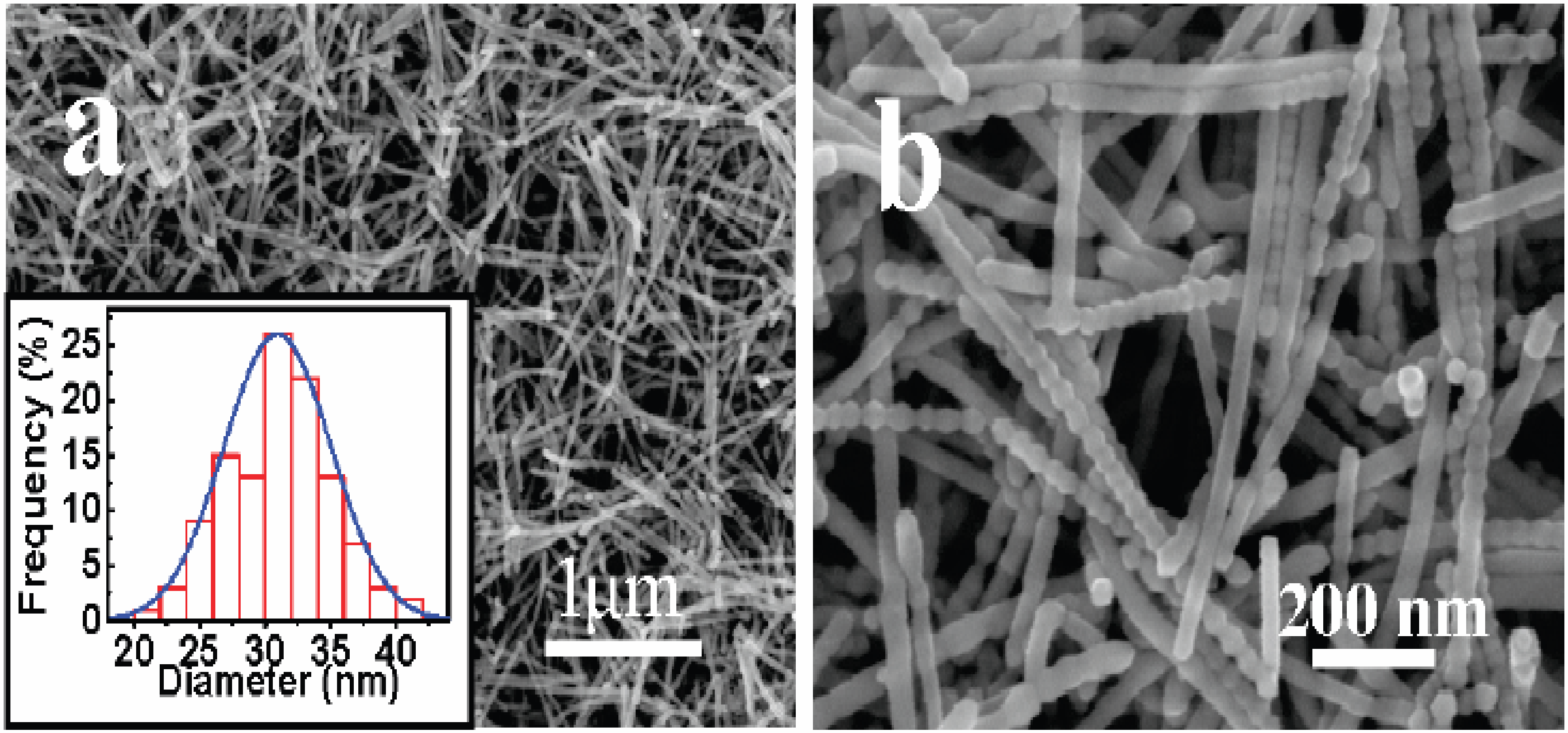
Synthesis of Pearl-Necklace-Shaped PbTe Nanowires

Te Nanowire solution
+ 0.268 g $Pb(NO_3)_2$ (0.8 mmol) $\xrightarrow{\text{453 K / 12 hrs.}}$ PbTe Nanowire

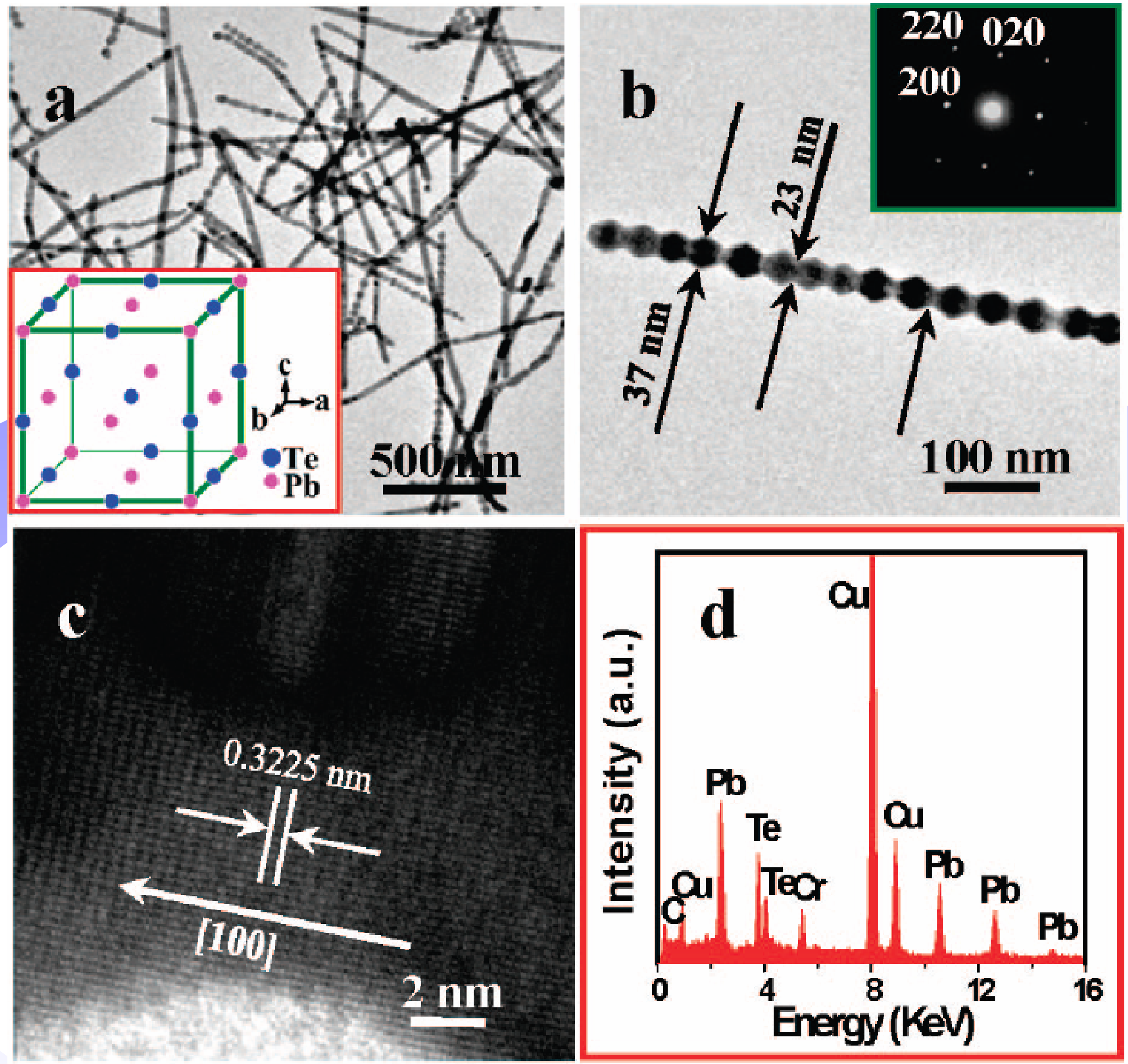
XRD characterization



XRD patterns of Te nanowires (a), and PbTe samples synthesized at different time intervals: (b) 1, (c) 3, (d) 6, (e) 9, and (f) 12 h.

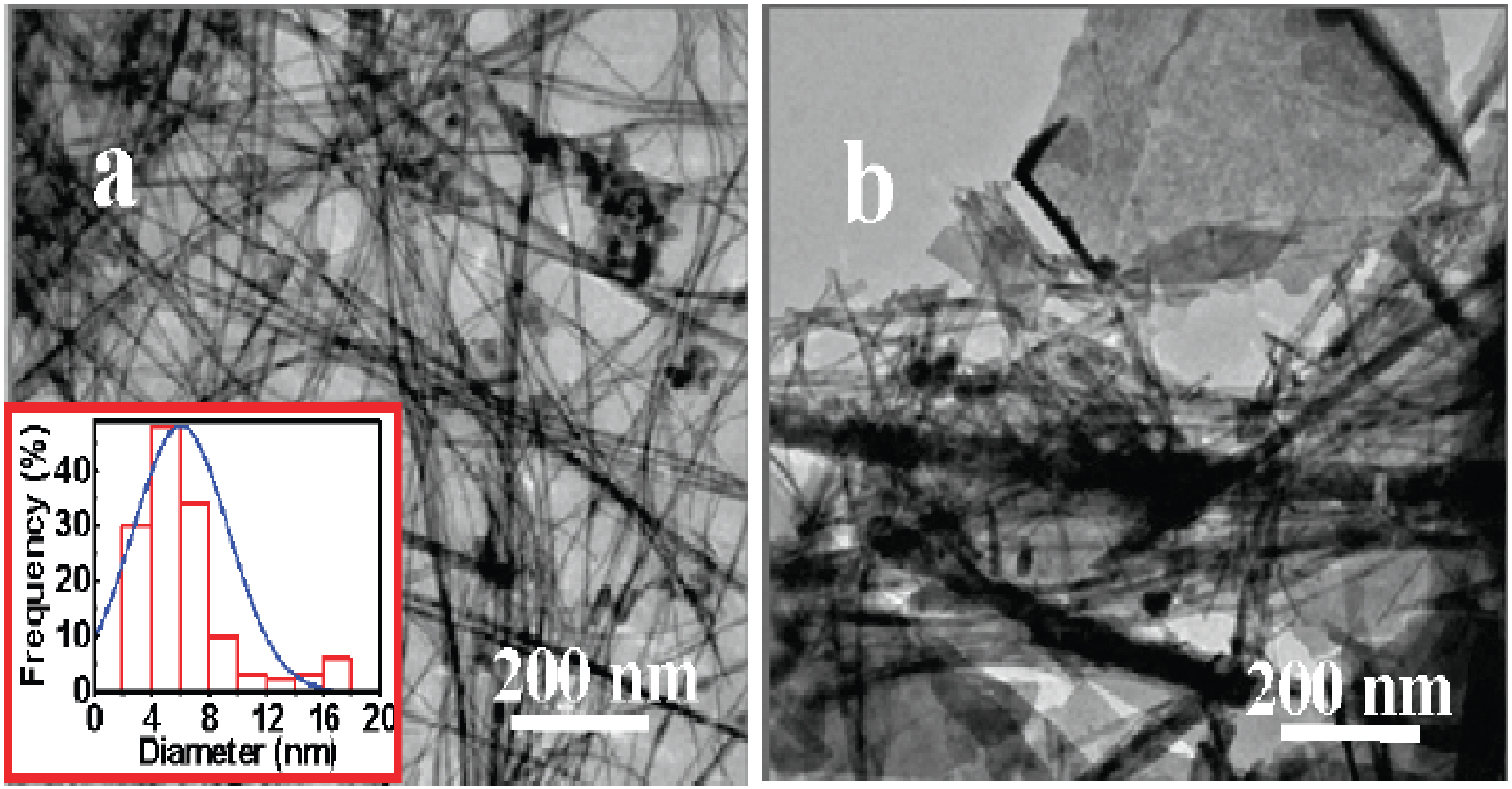


FESEM images of the pearl-necklace-shaped PbTe nanowires synthesized at 453 K for 12 h. (a) Low magnification; (b) high magnification. The inset of (a) is the diameter distribution of the PbTe nanowires.



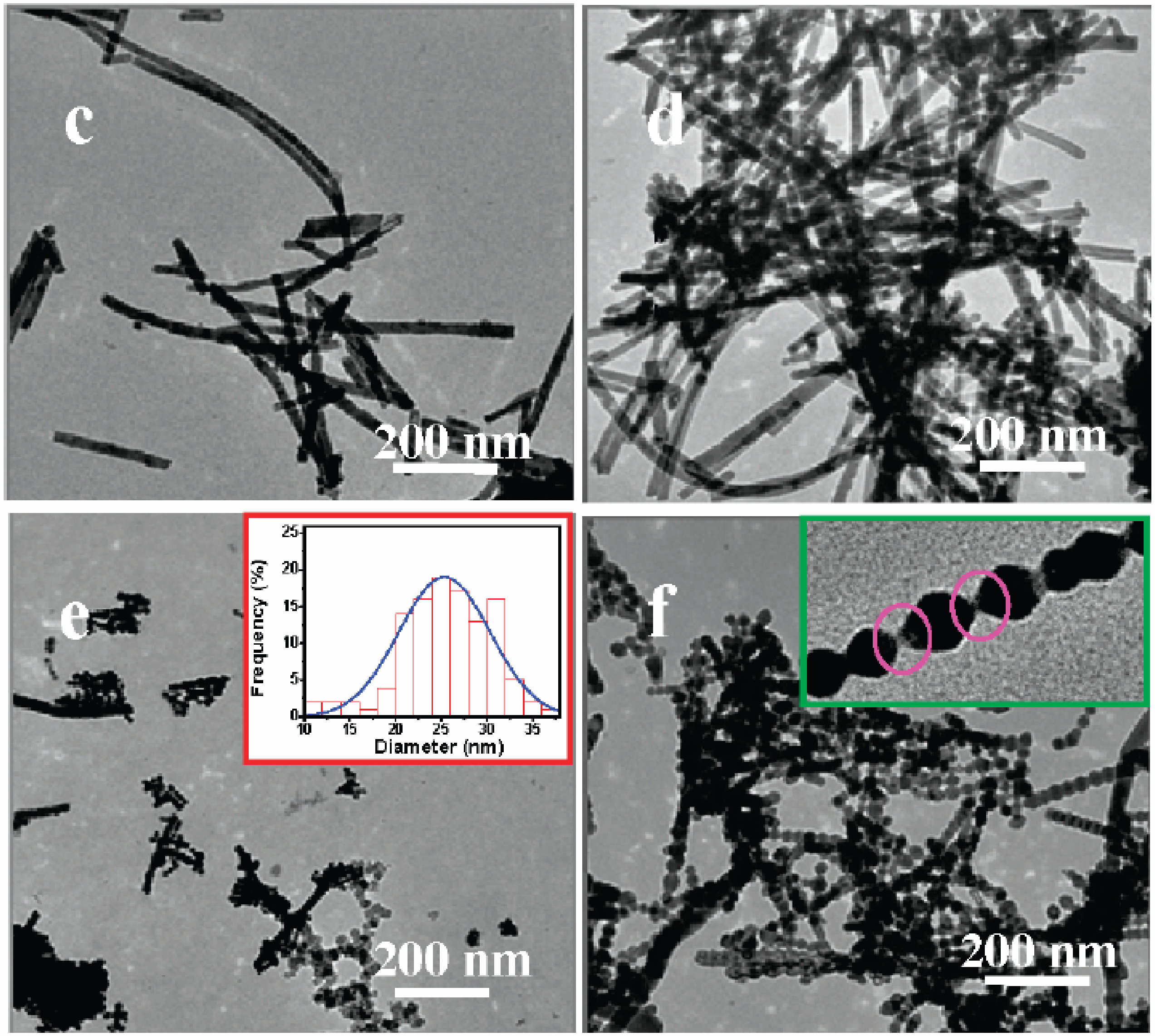
(a) TEM image of the PbTe nanowires. Inset: Unit cell of PbTe (b) TEM image of a single pearl-necklace-shaped nanowire with diameters of about 23 nm in the junction section and about 37 nm in the bead section. Inset: SAED pattern indexed for cubic PbTe. (c) HRTEM image taken from (b). (d) The EDX spectrum of the nanowires.

TEM Data



TEM images of the tellurium nanowires (a), Inset shows the diameter distribution of the tellurium nanowires and PbTe nanowires synthesized at room temperature (b).

Growth Mechanism



PbTe nanowires synthesized at 453 K at different time intervals: (c) 1, (d) 3, (e) 6, and (f) 9 h. The insets of (e) is the diameter distribution of the PbTe nanoparticles, respectively

Growth Mechanism

$$E^0_{Pb2+/Pb} = 0.126\ \text{V}$$

$$E^0_{N_2H_4/N_2} = -1.15\ \text{V}$$

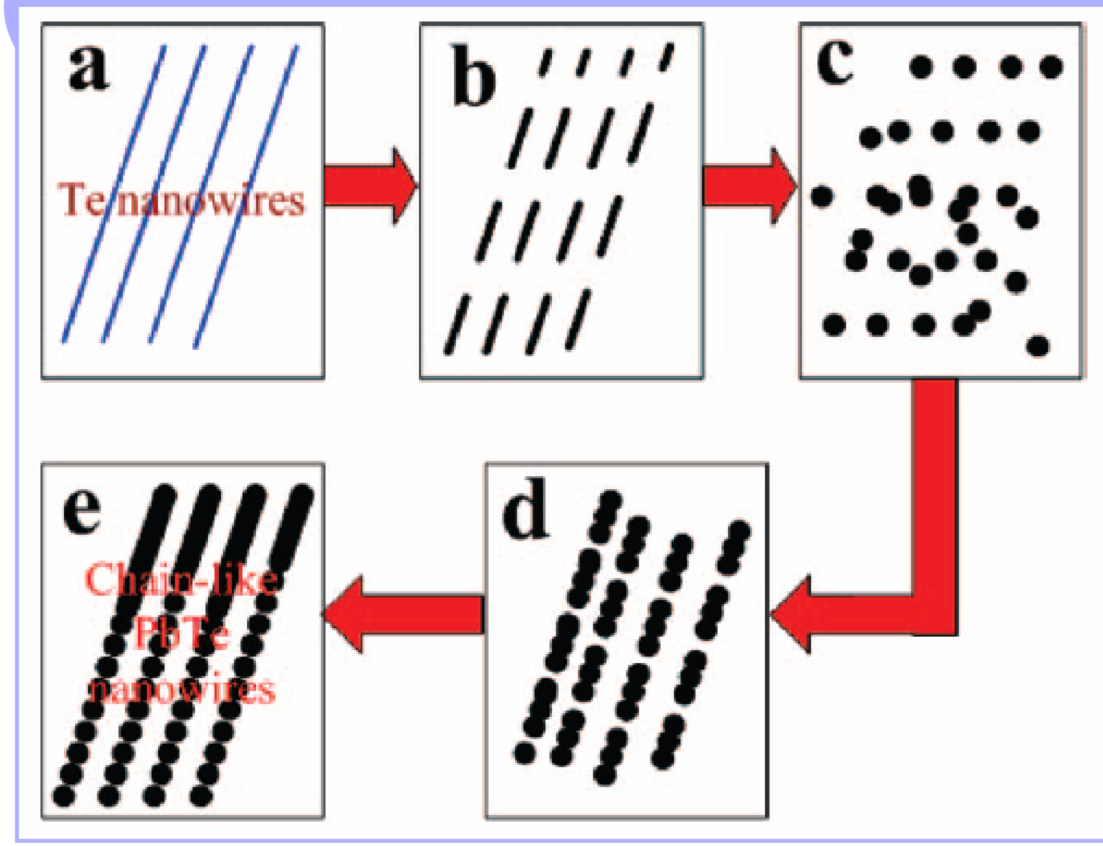
$$N_2H_4.H_2O + 4OH^- \longrightarrow N_2 + 5H_2O + 4e^-$$

$$2\ Pb^{2+} + N_2H_4 + 4\ OH^- \longrightarrow 2Pb + N_2 + 4\ H_2O$$

$$Pb + Te \longrightarrow PbTe$$

With increasing reaction duration the long tellurium nanowires will break and rupture into short sections and further into a large quantity of nanoparticles

Schematic presentation



Schematic presentation of tellurium nanowires (a) are transformed into short PbTe nanowires (b) and then into single nanoparticles (c); (d) pearl-necklace-shaped Pbte nanowires produced by oriented attachment of spherical nanoparticles and partially accompanied by Ostwald ripening to form partially smooth surface nanowires (e)

Oriented Attachment Mechanism

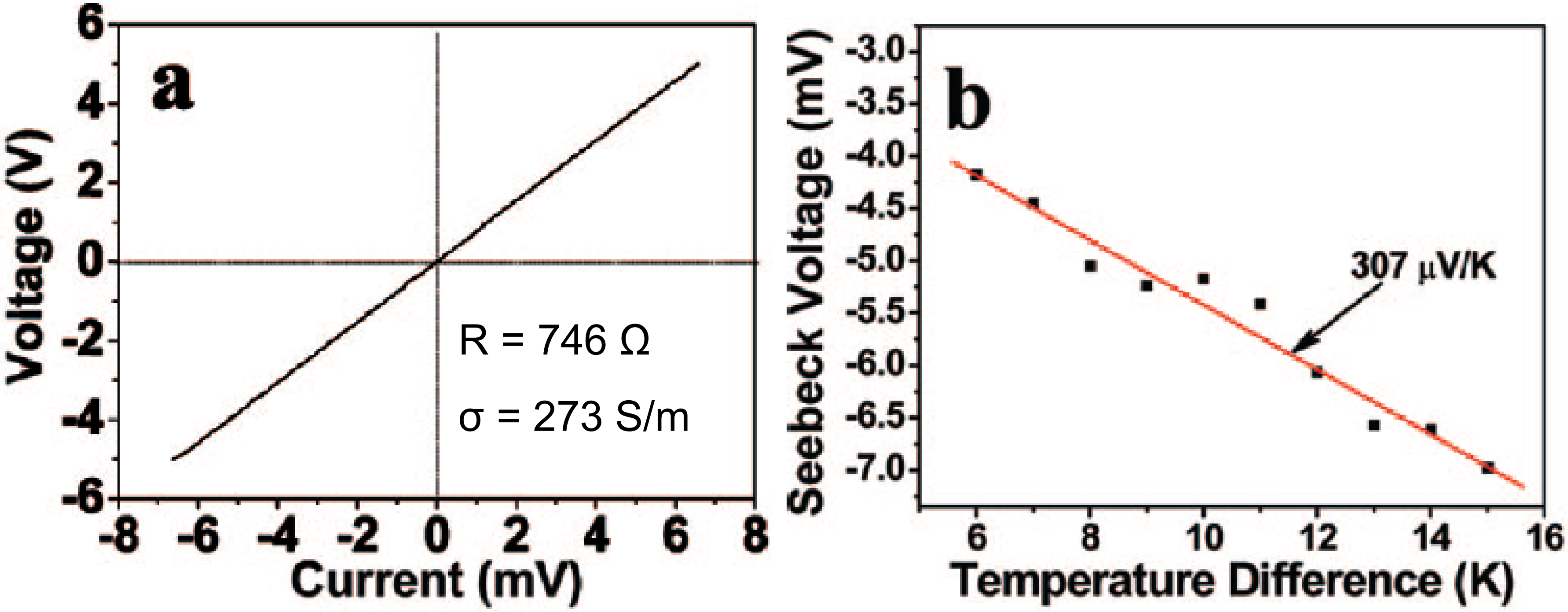
- ✓ Oriented attachment refers to the phenomenon that generates nanowires by attaching existing dot-shaped nanocrystals along a given crystal orientation.

- ✓ A dipole mechanism was invoked to explain the symmetry-breaking involved in the formation of the wire structures for semiconductors.

- ✓ For semiconductor nanomaterials, some faces will be terminated with the cation and others with the anion. This creates a net dipole moment on each nanoparticle that tends to orient the particles in a common direction.

- ✓ It is well documented that small PbSe nanocrystals are generally terminated by six {100} and eight {111} facets, and the largest permanent dipole moment was predicted along the (100) direction.

Thermoelectric Transport Measurement



(a) *I*-*V* characteristics obtained from a PbTe nanowire thin film. (b) Dependence of the Seebeck voltage as a function of temperature differences along the thermoelectric film.

Conclusions

- ✓Tellurium nanowires with diameters of 20-40 nm were prepared using polyvinyl pyrrolidone and Na_2TeO_3.

- ✓The pearl necklace-shaped PbTe nanowires were then successfully synthesized by the hydrothermal process using the tellurium nanowires as templates.

- ✓HRTEM, SAED, and SEM investigations show that PbTe nanowires are single crystalline and diameters of 20-40 nm, smaller than the 46 nm Bohr radius.

- ✓The growth process of the pearl-necklace-shaped PbTe nanowires can be reasonably explained by an oriented attachment mechanism.

- ✓Thermoelectric measurements show that the Seebeck coefficient has a 16% enhancement, whereas the electronic conductivity is lowered by two orders in the PbTe nanowire thin film when compared with that of the bulk PbTe.

Thank You