

# Chemical Transformations in Ultrathin Chalcogenide Nanowires

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ACS Nano, 2010, 4 (4), pp 2307–2319

26<sup>th</sup> June 2010

# Introduction

- Recently, chemical transformation of nanostructured materials has gained growing interest, due to the ability to transform existing materials to greatly diversify the compositions of nanostructured materials.
- It facilitates the synthesis of novel materials consisting of multiple components which may not be directly obtainable via a conventional synthesis.
- Furthermore, it might generate unprecedented shapes and unexpected crystal structures due to the mechanical stress accumulated during the transformation.
- Among various chemical transformations, Ion (cation/anion) exchange reactions have been demonstrated to be facile methods to modify the chemical composition of inorganic nanocrystals and have been extensively studied in the general areas of catalyst and thin film technology.
- A number of cations such as  $\text{Ag}^+$ ,  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$ , and  $\text{Cu}^+$  have been used to replace the  $\text{Cd}^{2+}$  ions in thin films of CdSe and CdS.

# Transformation through cation exchange

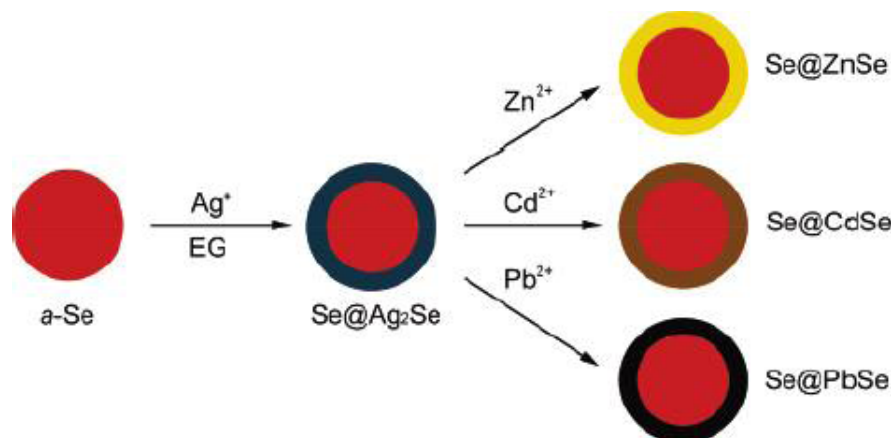
For the transformation of semiconductors, most studies have focused on the cation exchange of chalcogenides, whose crystal structures are determined by the frameworks of the chalcogen anions ( $S^{2-}$ ,  $Se^{2-}$ ,  $Te^{2-}$ ). The metal cations are relatively mobile in the anionic framework, making it possible to replace the cations under moderate reaction conditions.

- ❖ Alivisatos *et al.* demonstrated the cation exchange reaction between  $Ag_2Se$  and  $CdSe$  nanocrystals was completely reversible by adjusting the reaction conditions.



# Transformation through cation exchange

- ❖ Xia *et al.* showed that such transformation could be realized in mesoscale colloids.



- ❖ Son *et al.* investigated the effects of ion solvation and volume change on the morphology of resultant nanocrystals in the reactions of  $\text{CdE} \rightarrow \text{PdxEy}$  or  $\text{PtxEy}$  (E = S, Se, Te).
  - They found that stronger solvation of  $\text{Cd}^{2+}$  lowered the activation energy for the transformation and facilitated the exchange between  $\text{Cd}^{2+}$  cations and  $\text{Pd}^{2+}$  or  $\text{Pt}^{2+}$  cations.
  - It was observed that a severe volume reduction could result in hollow nanocrystals, while a volume increase could break the structure into smaller pieces.

# Transformation through cation exchange

- ❖ Xia *et al.* demonstrated successful transformations of  $\text{Ag}_2\text{Se}$  into  $\text{CdSe}$  while keeping the single crystallinity of the nanowires.
- ❖ Yu *et al.* showed that ultrathin  $\text{Te}$  nanowires could be converted into  $\text{CdTe/PbTe}$  nanowires or  $\text{Pt/Pd}$  nanowires/nanotubes.

The governing factors for the transformations can be summarized as the following:

- (i) the thermodynamic parameters that determine the transformation direction
- (ii) the kinetics of a transformation (activation barrier),
- (iii) the effect of mechanical stress on retaining the initial shape, and
- (iv) the mechanisms of transformations (the way of diffusion for foreign cations)

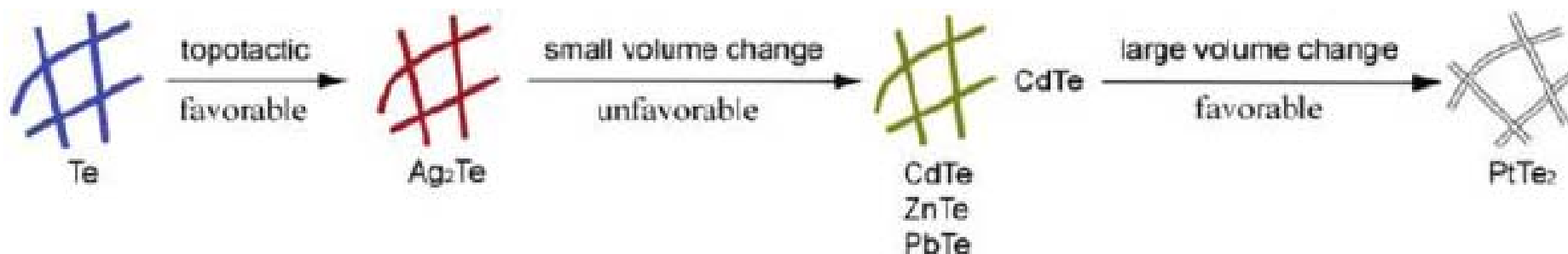
Alivisatos *et al.* first postulated the solubility product of the ionic solids in the reaction medium may determine the thermodynamic direction of transformations.

# In this paper...

A systematic study of chemical transformations in nanowires, started with ultrafine, single-crystalline Te nanowires.

Ultrathin nanowires have recently been a major theme of intensive research due to their high surface-to-volume ratio and unique electronic or thermal behaviors. The large surface area and enhanced colloidal dispersion have enabled their use in sensors, catalytic supports, and solution-processable electronics.

Chemical transformations in this study can be divided into three groups as shown in the scheme.



# Growth of Te nanowires

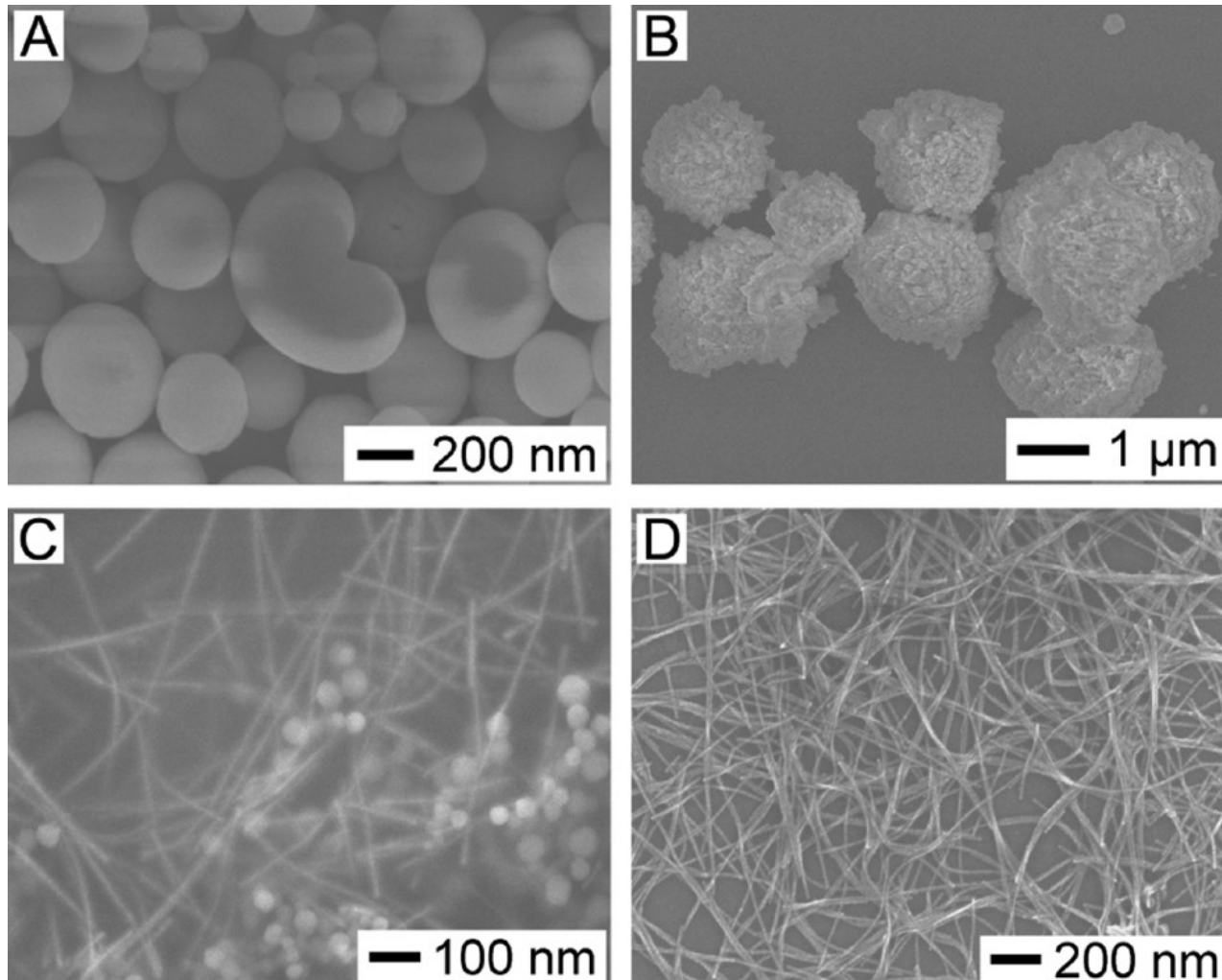


Figure 1. SEM images showing the evolution of ultrathin Te nanowires: (A) tellurium oxide colloids formed right after the introduction of aqueous telluric acid into an aqueous solution of hydroxyl amine at room temperature, (B) partial dissolution of tellurium oxides at about 50 °C, (C) nucleation and growth of ultrathin t-Te nanowires in boiling water, and (D) the final product of ultrathin and long Te nanowires after 12 h of reaction.



# Te nanowires

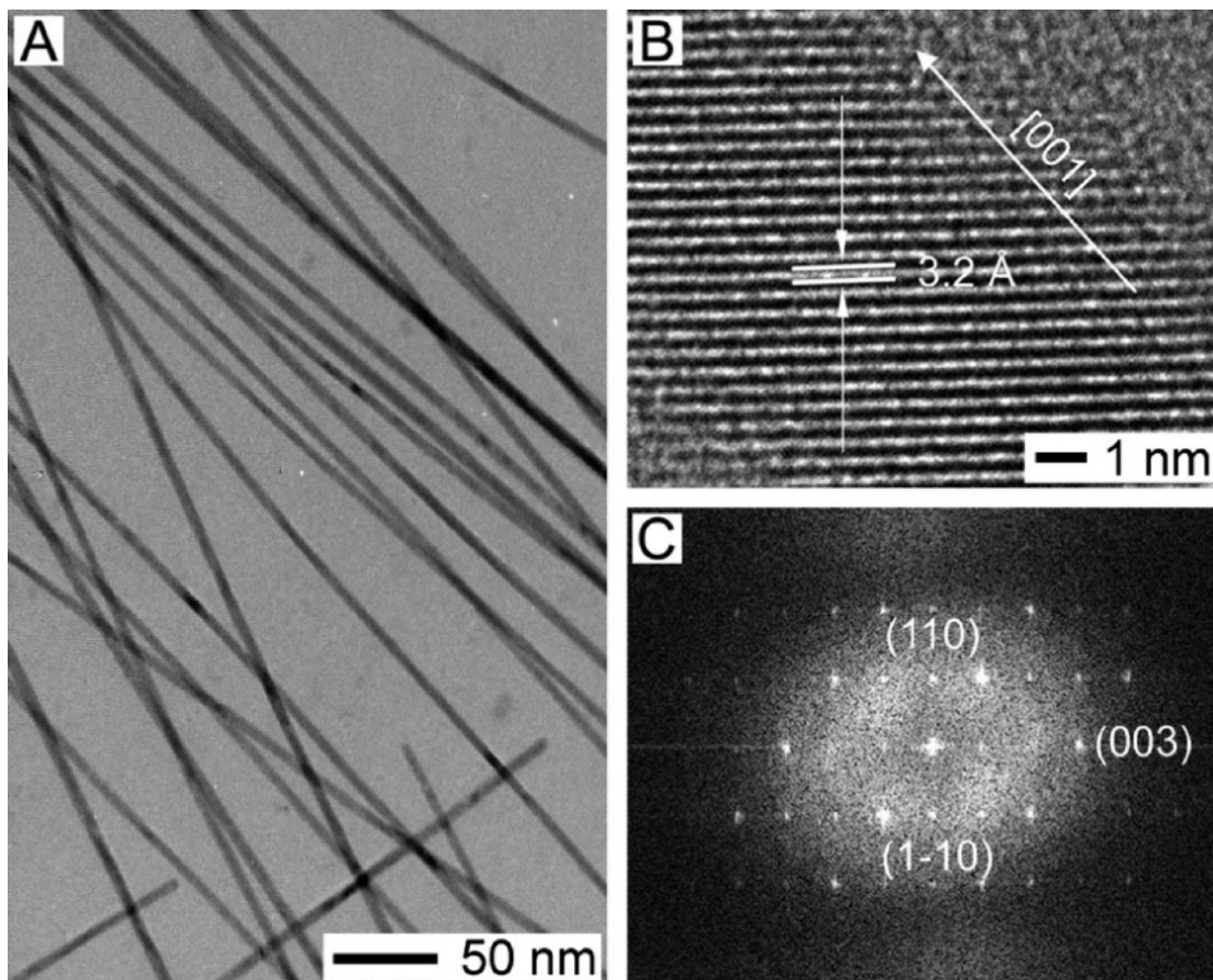
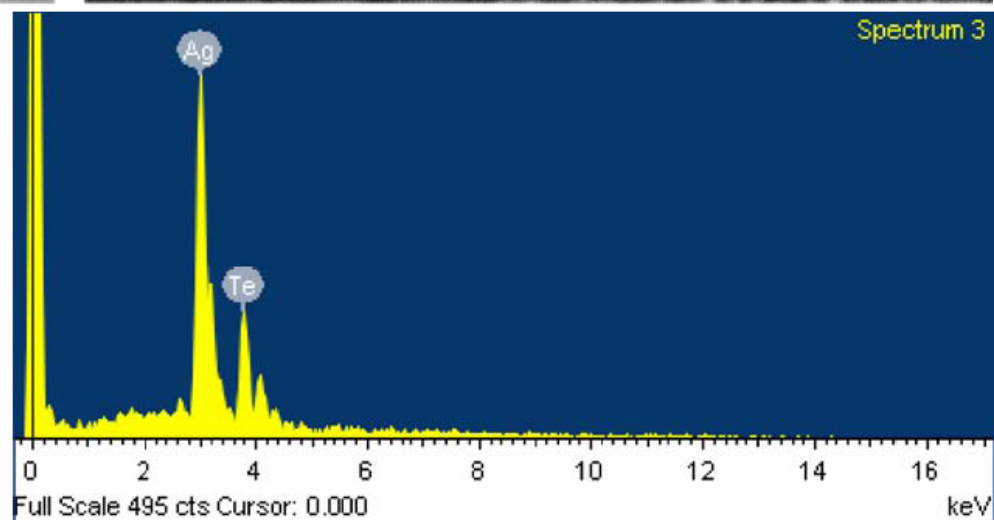
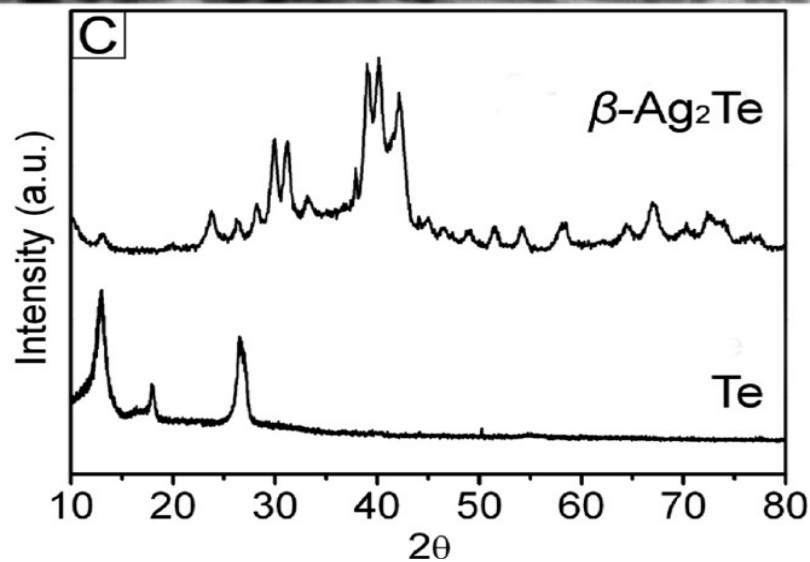
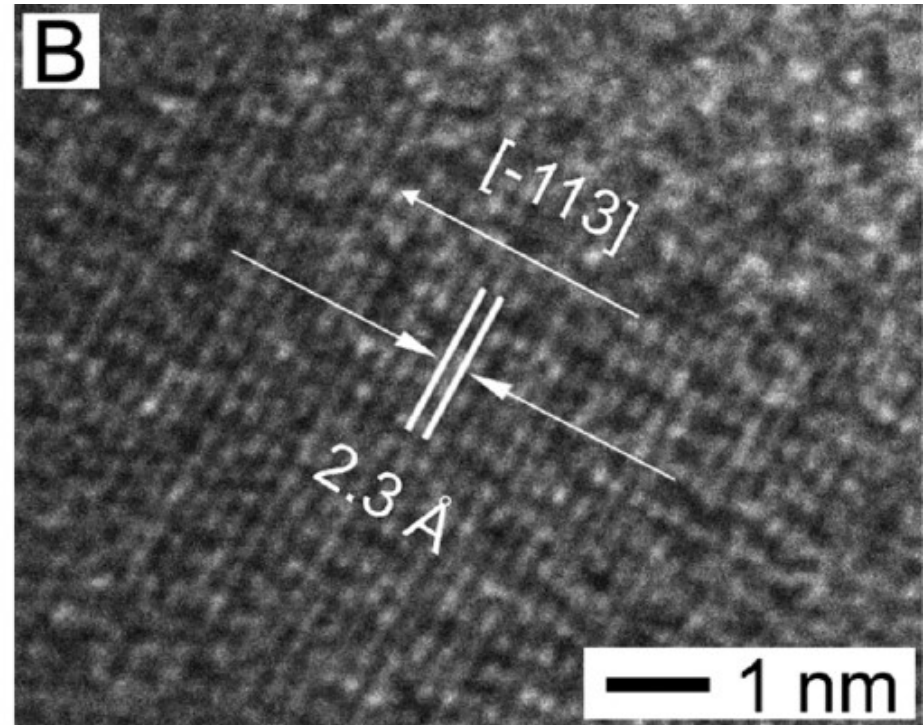
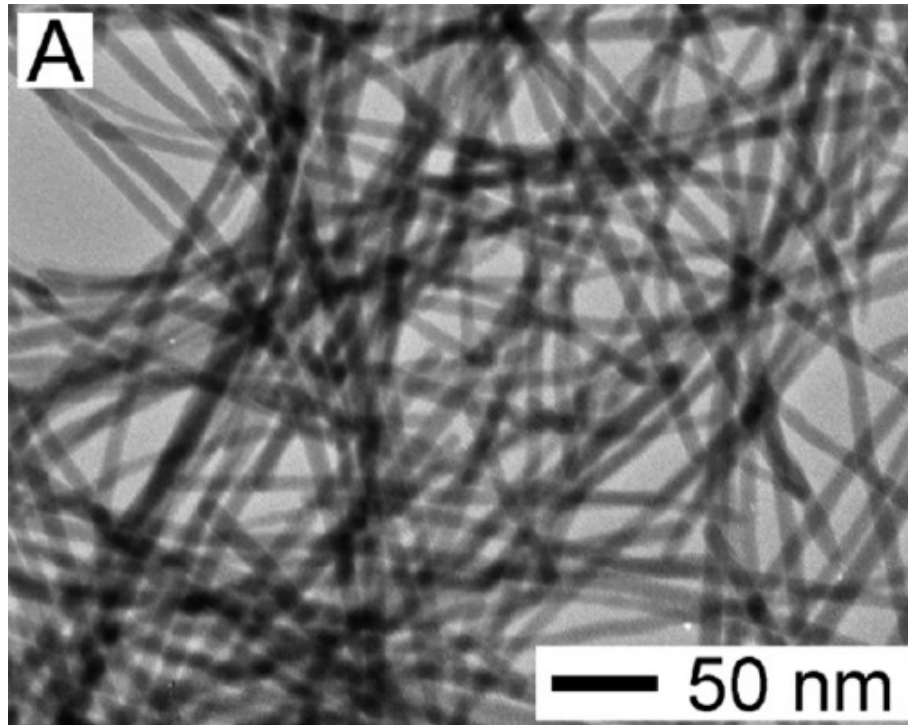


Figure 2. (A) TEM image of t-Te nanowires synthesized in boiling water. (B) High-resolution TEM (HR-TEM) image of the Te nanowire, which could be indexed as a hexagonal crystal structure with a lattice fringe spacing of 3.2 Å. The growth direction was along  $[001]$ . (C) Fourier transformed pattern obtained from the HR-TEM image.



# Transformation of Te to $\text{Ag}_2\text{Te}$ nanowires



# Structural transformation

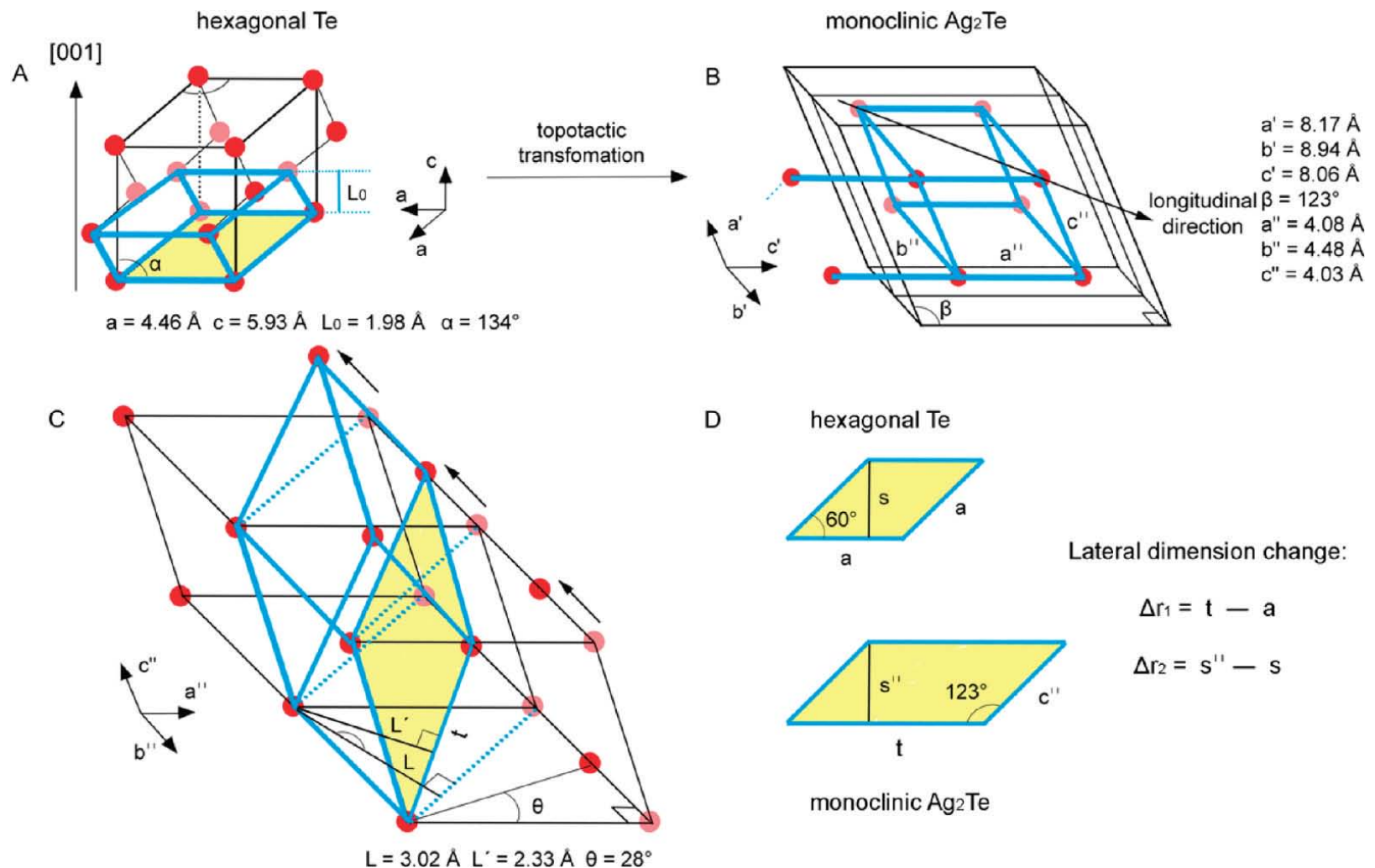


Figure 5. Schematic illustration of the crystal structures. (A,B) Topotactic transformation from the helical structure of hexagonal Te into monoclinic  $\text{Ag}_2\text{Te}$  in a way that all of the lattice parameters changed. (C) Te atoms (red circles) along the  $a''$ -axis are located in a distorted way, being tilted by  $28^\circ$  from the  $a'$ -axis (Te atoms in light-red circles). (D) Changes to lateral dimensions during the transformation from Te to  $\text{Ag}_2\text{Te}$ .

# Transformation of Te to $\text{Ag}_2\text{Te}$ nanorods

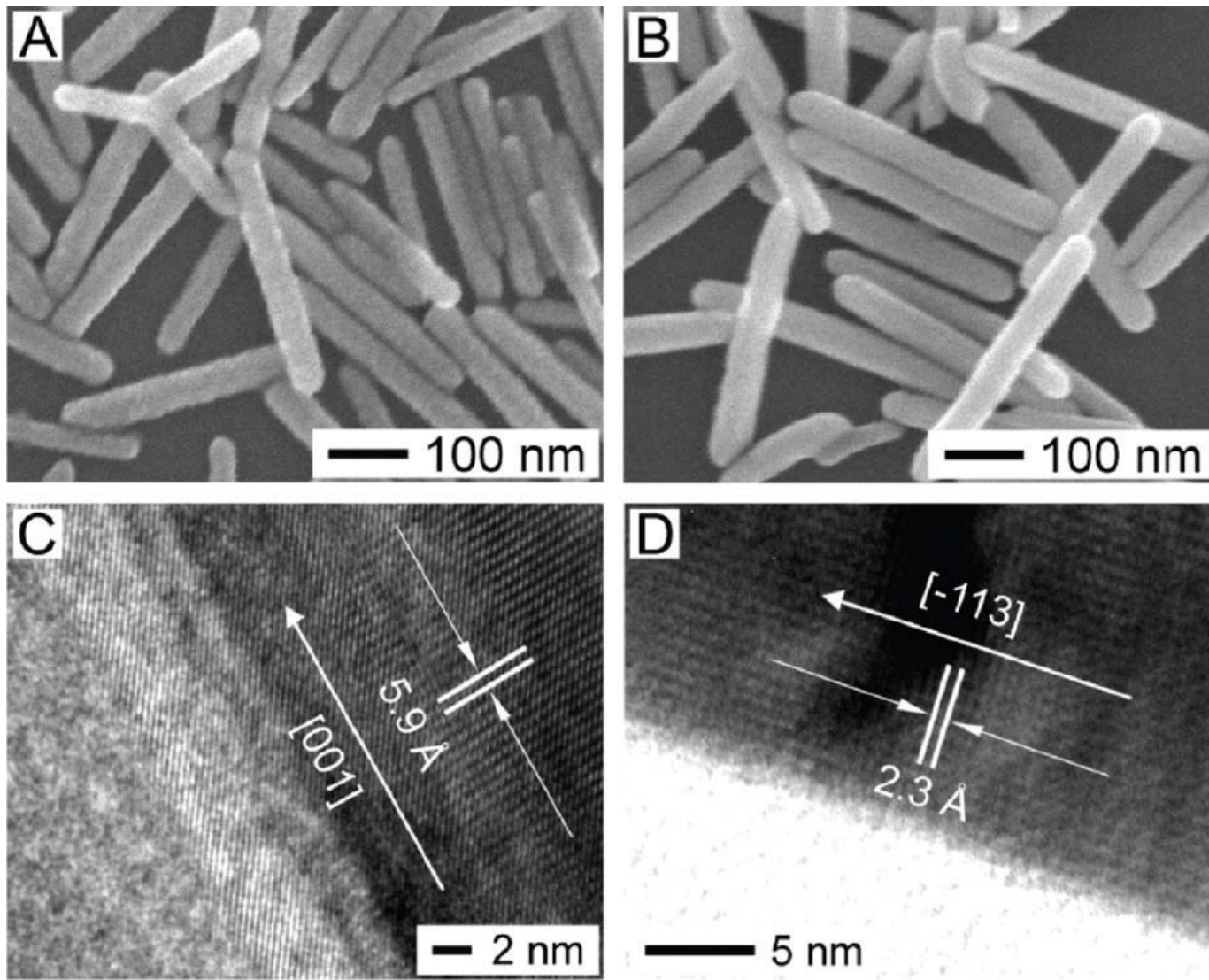


Figure 6. SEM and HR-TEM images of (A,C) Te nanorods synthesized in EG at 100 °C for 2 h and (B,D)  $\text{Ag}_2\text{Te}$  nanorods derived from the as-synthesized Te nanorods through a topotactic reaction with  $\text{AgNO}_3$  in EG.

# Favorable direction in Cation exchange reactions

According to Son et al, three important factors should be considered to fully take advantage of the cation-exchange reaction: solubility of ionic solids, crystal structure, and mechanical stress generated by volume change during the reaction.

The difference in solubility product of the reactants and products can be chosen as the first criterion to determine the thermodynamically favorable direction in the cation exchange.

Solubility product,  $K_{sp}$ , of ionic solid is referred to as an equilibrium constant between an ionic solid and its dissolved state in solution. The equilibrium solubility constant ( $K$ ) is a product of activities of each constituent chemical.

When the solubility or concentration of the salt is very low, which is the case for most inorganic synthesis, the activity can be taken as the concentration of the constituting ions.

Solubility product is related to the free energy change of a solution ( $\Delta G = RT \ln K_{sp}$ ), which leads to a conclusion that an ionic solid with a relatively high  $K_{sp}$  value goes through cation exchange to form another ionic solid with a relatively low  $K_{sp}$ .



# Favorable direction in Cation exchange reactions

When the size of materials goes down to nanoscale, the solubility is greatly increased. The effect can be quantified as follows

$$\log K_{sp}^* = \log K_{sp,bulk} + 2\gamma A_m / [3 \log(RT)]$$

where  $K_{sp}$ ,  $\gamma$ , and  $A_m$  are the solubility product, the surface tension, and the molar surface area (in  $m^2/mol$ ) of the solute in the order.

Therefore, ultrathin nanowires or nanocrystals should possess enhanced solubility compared with bulk materials, which should result in the fast reactions as observed.

The existence of complexation species to the constituting ions can considerably increase the solubility without changing the solubility product itself because the complexed form does not enter the solubility equilibrium.

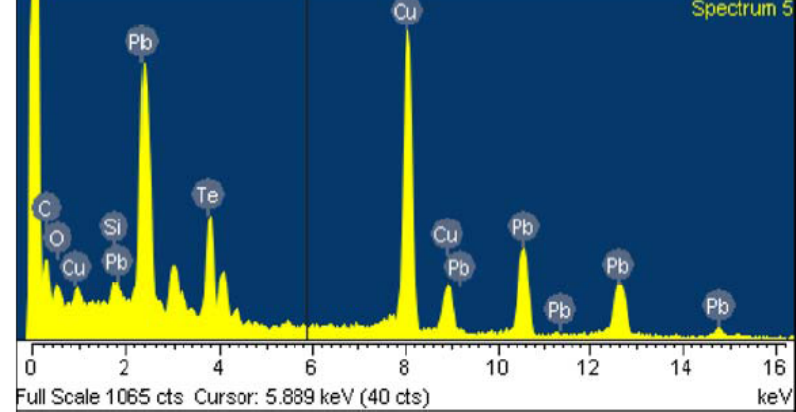
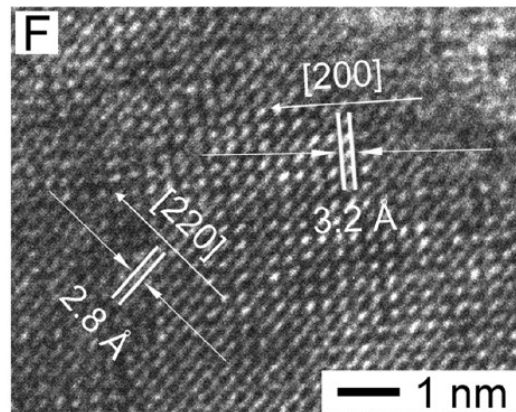
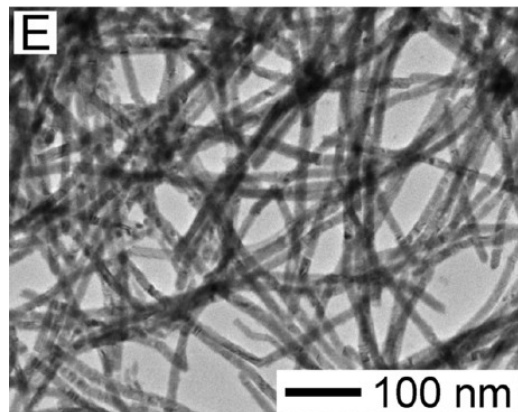
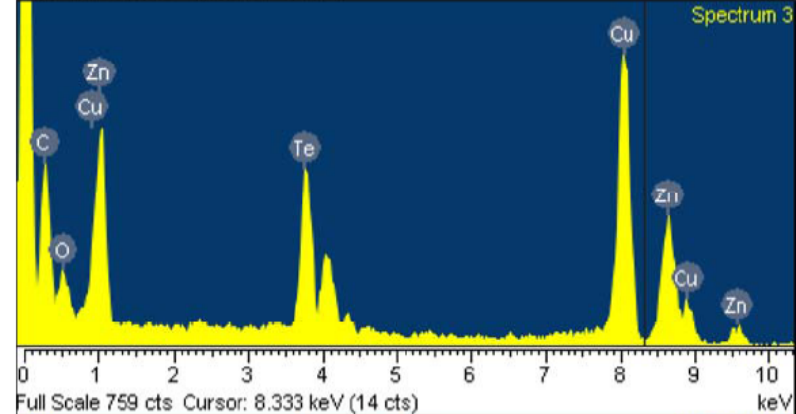
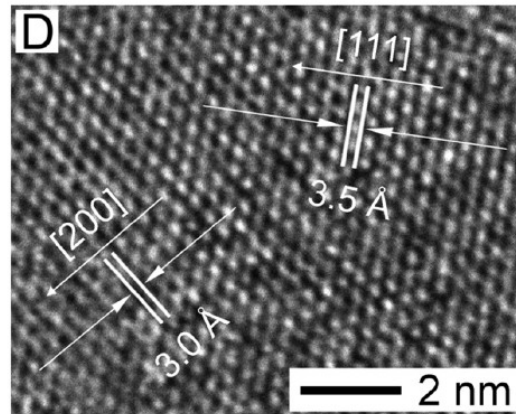
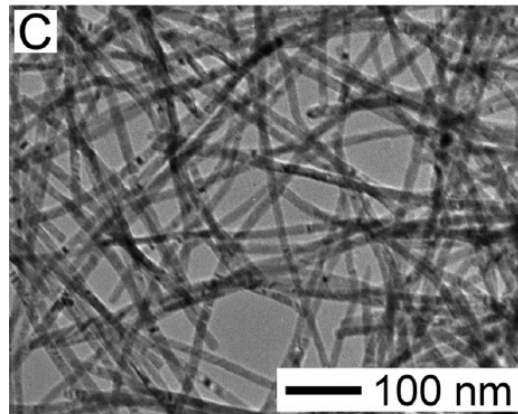
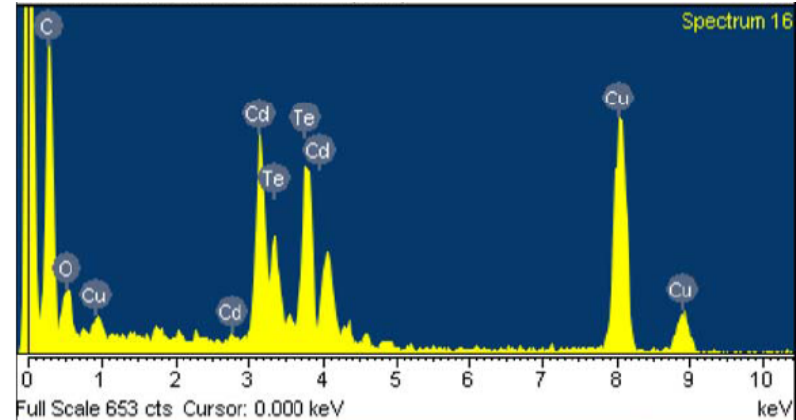
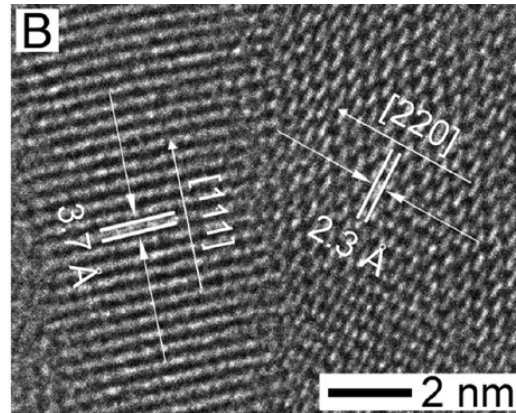
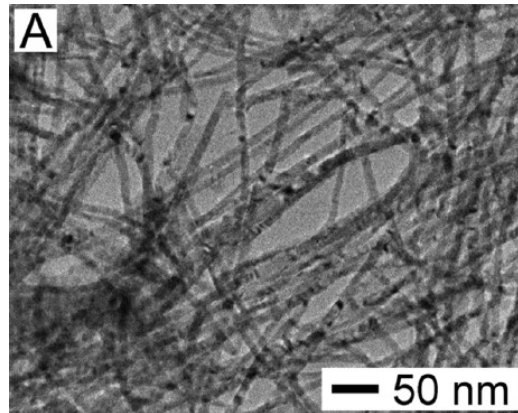
# Solubility product in water

Solid	E = S	E = Se	E = Te
Ag <sub>2</sub> E	$3 \times 10^{-50}$	$1 \times 10^{-54}$	N.A.
Bi <sub>2</sub> Te <sub>3</sub>	$1 \times 10^{-100}$	$1 \times 10^{-130}$	N.A.
CdE	$1 \times 10^{-28}$	$4 \times 10^{-35}$	$1 \times 10^{-42}$
CuE	$5 \times 10^{-36}$	$2 \times 10^{-40}$	N.A.
HgE	$6 \times 10^{-53}$	$4 \times 10^{-59}$	N.A.
NiE	$1 \times 10^{-21}$	$2 \times 10^{-26}$	N.A.
PbE	$1 \times 10^{-28}$	$1 \times 10^{-37}$	N.A.
PtE	$9.9 \times 10^{-74}$	N. A.	N.A.
SbE	$2 \times 10^{-93}$	N.A.	N.A.
SnE	$1 \times 10^{-26}$	$5 \times 10^{-34}$	N.A.
ZnE	$3 \times 10^{-25}$	$1 \times 10^{-27}$	N.A.

TABLE 1. Solubility Product Data of Various Metal Chalcogenides in water

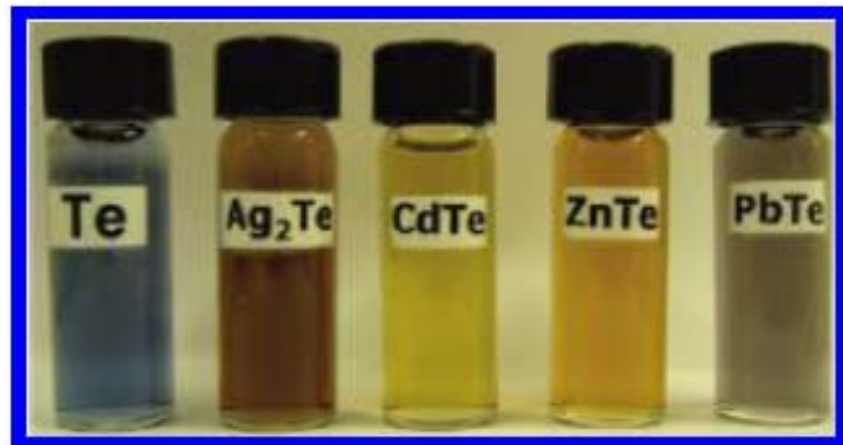
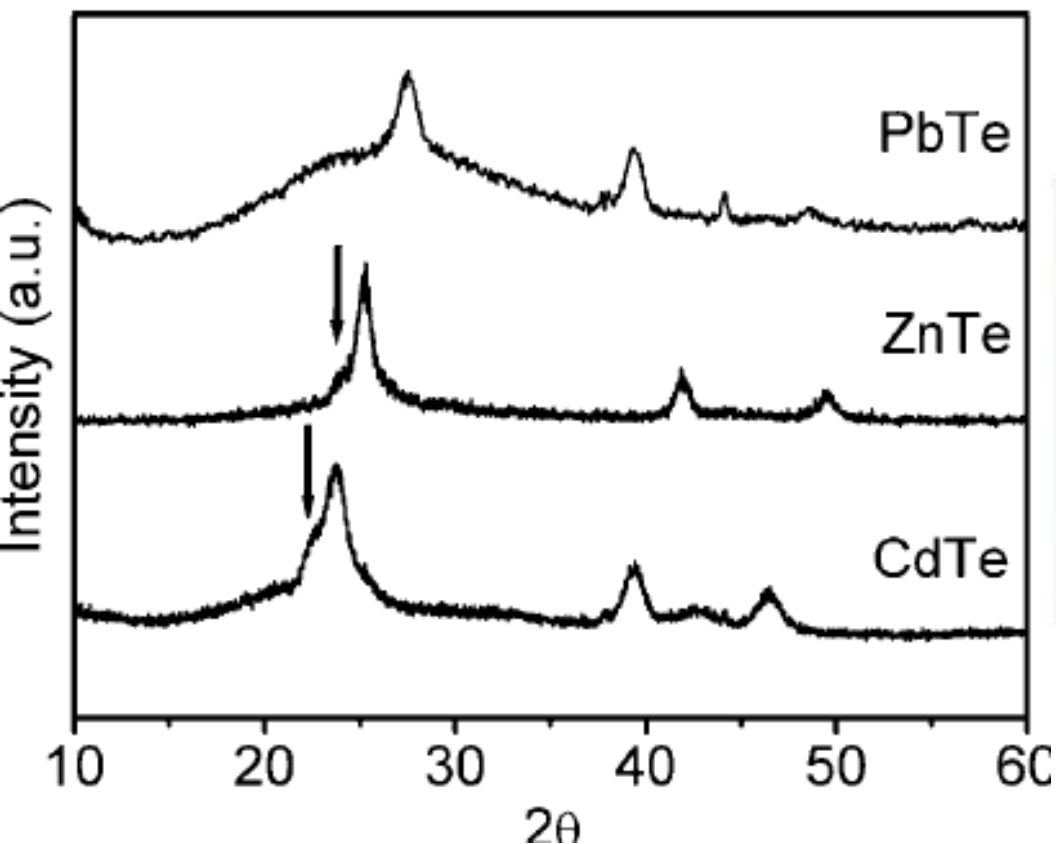
Solubility products of metal chalcogenides have a lower value as the ionic radius of chalcogen increases:  $K_{sp}(\text{MxSy}) > K_{sp}(\text{MxSe}) > K_{sp}(\text{MxTe})$ .

# Transformation of $\text{Ag}_2\text{Te}$ to $\text{CdTe}$ , $\text{ZnTe}$ and $\text{PbTe}$ nanowires





# Transformation of $\text{Ag}_2\text{Te}$ to $\text{CdTe}$ , $\text{ZnTe}$ and $\text{PbTe}$ nanowires

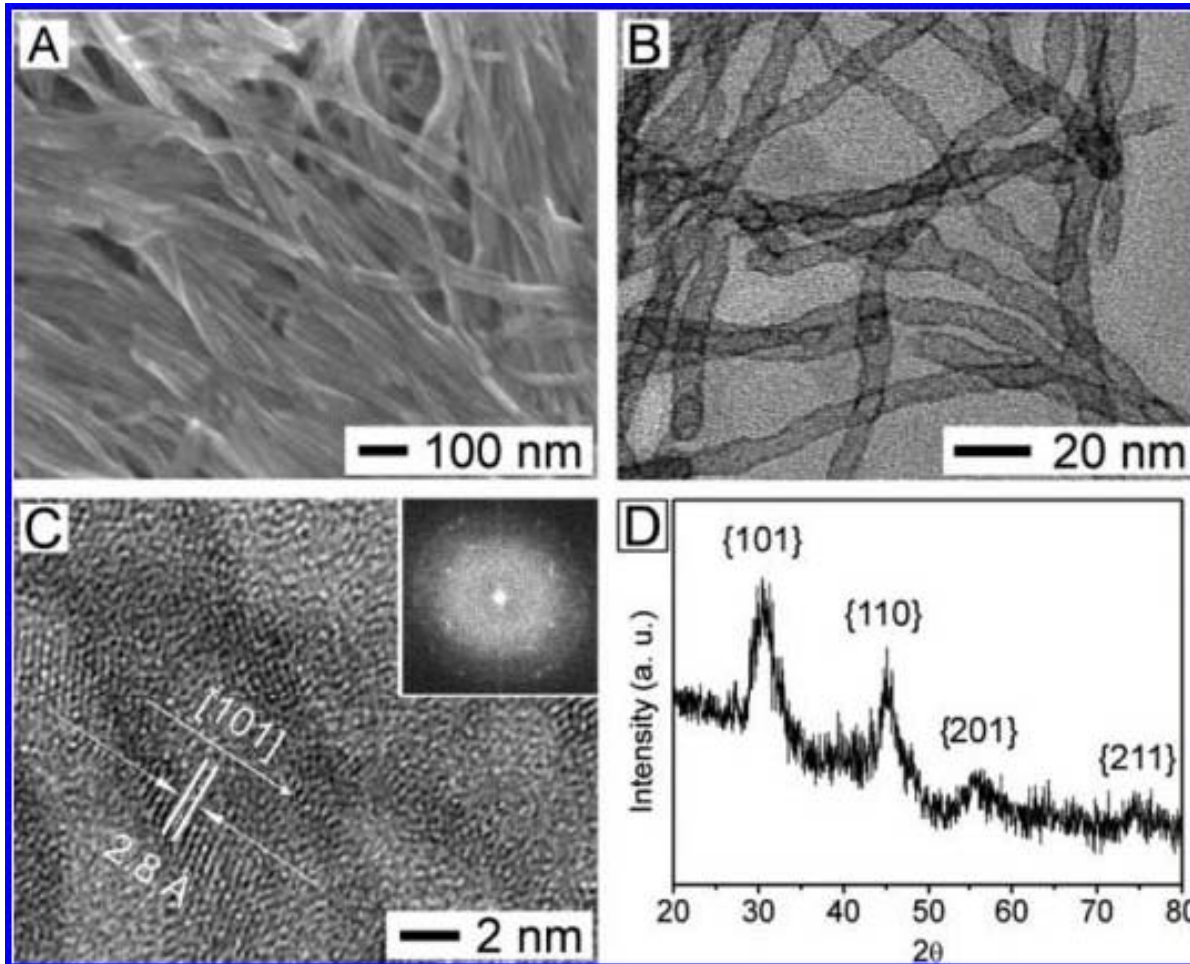


# Transformation of Ag<sub>2</sub>Te to PtTe<sub>2</sub> nanotubes

**TABLE 3. Structure, Lattice Parameters, and Volume Change during Chemical Transformations in This Study**

initial material		final product	$\Delta V/V$
Te trigonal $a = 4.46, c = 5.93$ Ag <sub>2</sub> Te	Ag <sub>2</sub> Te	monoclinic $a = 8.17, b = 8.94, c = 8.06$	1.009
	CdTe	zinc blende $a = 6.48$	0.0025
		wurtzite $a = 4.57, c = 7.44$	0.0036
	ZnTe	zinc blende $a = 6.10$	−0.163
		wurtzite $a = 4.31, c = 7.09$	−0.1599
	PbTe	cubic $a = 6.45$	−0.0076
		orthorhombic $a = 4.7, b = 12.1, c = 4.1$	−0.1413
CdTe	PtTe <sub>2</sub>	hexagonal $a = 4.02, c = 5.22$	−0.462

# Transformation of CdTe to PbTe nanowires



(A) SEM and (B) TEM images of PtTe<sub>2</sub> nanotubes derived from CdTe nanowires through a cation-exchange reaction in methanol at room temperature. (C) HR-TEM image of a PtTe<sub>2</sub> nanotube indexed as the hexagonal phase with lattice spacing of 0.28 nm along the [101] direction. The inset shows the Fourier transformed ring pattern of PtTe<sub>2</sub> nanotubes. (D) XRD of the PtTe<sub>2</sub> nanotubes. All peaks were indexed to a hexagonal crystal structure for PtTe<sub>2</sub>.

# Conclusions

First, the solubility product of ionic solids can be a rough, but useful, criterion to anticipate if the transformation is thermodynamically favorable or not. The transformations from CdTe into  $\text{PtTe}_2$  were found favorable in pure solvents because the solubility products of  $\text{PtTe}_2$  were much lower than that of CdTe.

Meanwhile, the transformations from  $\text{Ag}_2\text{Te}$  into CdTe, ZnTe, and PbTe were unfavorable in pure solvents. The reactions required complexation additives to initiate the conversion.

Second, the morphological preservation of reactant nanowires is dependent on the dimensional change in length direction rather than total volume change. The small amount of volume change from  $\text{Ag}_2\text{Te}$  nanowires into CdTe, ZnTe, and PbTe led to well-preserved single crystalline nanowires.