

## Research Article

# Hydrothermal Synthesis and Mechanism of Unusual Zigzag $\text{Ag}_2\text{Te}$ and $\text{Ag}_2\text{Te}/\text{C}$ Core-Shell Nanostructures

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A single step surfactant-assisted hydrothermal route has been developed for the synthesis of zigzag silver telluride nanowires with diameter of 50–60 nm and length of several tens of micrometers. Silver nitrate ( $\text{AgNO}_3$ ) and sodium tellurite ( $\text{Na}_2\text{TeO}_3$ ), are the precursors and polyvinylpyrrolidone (PVP) is used as surfactant in the presence of the reducing agent, that is, hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ). In addition to the zigzag nanowires a facile hydrothermal reduction-carbonization route is proposed for the preparation of uniform core-shell  $\text{Ag}_2\text{Te}/\text{C}$  nanowires. In case of  $\text{Ag}_2\text{Te}/\text{C}$  synthesis process the same precursors are employed for Ag and Te along with the ethylene glycol used as reducing agent and glucose as the carbonizing agent. Morphological and compositional properties of the prepared products are analyzed with the help of scanning electron microscopy, transmission electron microscopy, and energy dispersive X-ray spectroscopy, respectively. The detailed formation mechanism of the zigzag morphology and reduction-carbonization growth mechanism for core-shell nanowires are illustrated on the bases of experimental results.

## 1. Introduction

The use of 1D nanostructures for advancement in nanoelectronic and optoelectronic devices requires great diversity of structures and needs different morphologies to be synthesized in either bulk form or in thin films. The recent recommendation of new geometric configurations for smart materials has made it essential to set up nanoscale building blocks in axial or radial way that allow another dimension to tune their properties [1–3]. For this reason, the zigzag morphology possessing breaks in the lattice periodicity at junctions exhibits another class of nanostructures that can propose confinement effect and increased excitonic behaviour. Similarly, the core-shell nanostructures present a formal protocol to realize the aim of functional nanomaterials, integrated with multiple roles in single crystal. The isolation of the core from the surroundings can be utilized to prepare such materials or devices whose properties are different from the bare nanomaterials. The shell can be used to reduce the chemical reactivity

of the surface to modify its optical properties or to devise some nanoscale devices with specific electrical functionality. Especially the functionalized carbonaceous nanowires have appealed attention for potential applications.

The monoclinic structure of  $\text{Ag}_2\text{Te}$  is a narrow band gap material with high electron mobility. Until now different morphologies regarding  $\text{Ag}_2\text{Te}$  have been synthesized. For example, the rod-like nanostructure of  $\text{Ag}_2\text{Te}$  was obtained with the use of Te nanorods as the template reagents [4].  $\text{Ag}_2\text{Te}$  nanotubes were hydrothermally synthesized with the use of sodium tellurite and silver nitrate as the precursors in the presence of hydrazine and ammonia solution [5]. Samal and Sandeep have reported the room temperature synthesis method for synthesizing  $\text{Ag}_2\text{Te}$  nanowires [6]. Most recently, another facile hydrothermal route is reported for  $\text{Ag}_2\text{Te}$  NWs [7]. The same group worked on the morphological evolution and growth mechanism of its nanostructures by employing ammonia as a pH regulator and hydrazine as the reducing agent [8].

To the best of our knowledge, synthesis of zigzag  $\text{Ag}_2\text{Te}$  nanowires and core-shell  $\text{Ag}_2\text{Te}$  nanowires with carbonaceous shell has not been achieved so far. Herein, on the bases of simple hydrothermal conditions we demonstrate that for the synthesis of zigzag  $\text{Ag}_2\text{Te}$ , hydrazine is used as the reducing agent and PVP is employed as the surfactant. In case of core-shell nanowires D-glucose and EG have been utilized as the carbonizing and reducing agent. Hence, we believe that this discovery of formation of new morphologies of 1D nanostructures of  $\text{Ag}_2\text{Te}$  could promote further advances and potential applications.

## 2. Materials and Methods

**2.1. Synthesis of Zigzag  $\text{Ag}_2\text{Te}$  Nanowires.** For the zigzag  $\text{Ag}_2\text{Te}$  nanostructures the materials used include  $\text{Na}_2\text{TeO}_3$  (98%),  $\text{AgNO}_3$  (99.8%), polyvinylpyrrolidone (M.W. 58, 99%), and  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (85%). All of these reagents were directly used in the experiment without any further purification. The synthesis process involves a simple hydrothermal route. In a typical experiment 2 mmol of  $\text{AgNO}_3$  was dissolved in 50 mL of deionized water. After stirring for several minutes 1 mmol of  $\text{Na}_2\text{TeO}_3$  was dissolved in the solution. Then the 0.5 g of PVP was added along with the dropwise addition of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ . A mixed solution was dropped in 100 mL Teflon lined autoclave, followed by heating at  $240^\circ\text{C}$  for 24 hrs. After heating for predefined duration, the autoclave was allowed to cool at room temperature. The precipitates were centrifuged and washed with ethanol and distilled water several times and finally dried at  $60^\circ\text{C}$  for 12 hrs.

**2.2. Synthesis of  $\text{Ag}_2\text{Te}/\text{C}$  Nanowires.** In case of  $\text{Ag}_2\text{Te}/\text{C}$  core-shell nanostructures sodium tellurite ( $\text{Na}_2\text{TeO}_3$ ), ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ), silver nitrate ( $\text{AgNO}_3$ ), and D-glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) were used in typical hydrothermal synthesis process. 0.34 g of  $\text{AgNO}_3$  and 0.22 g of  $\text{Na}_2\text{TeO}_3$  and 0.3 g of  $\text{C}_6\text{H}_{12}\text{O}_6$  were dissolved in 10 mL of deionized water. Then 20 mL of ethylene glycol was added and stirred continuously. The final solution was shifted into a 100 mL Teflon lined autoclave. The autoclave was maintained at  $180^\circ\text{C}$  for 18 hrs. After the required time the autoclave was left to cool naturally at the room temperature. Final product was centrifuged with deionized water and ethanol and was then dried at  $60^\circ\text{C}$  for 12 hrs.

The size and the morphology of the prepared  $\text{Ag}_2\text{Te}$  nanostructures were characterized using scanning electron microscopy (SEM) (Hitachi S-4800), provided with X-ray energy dispersive spectrum analysis (EDS). The crystalline structure was characterized by using the TEM and high resolution TEM (HRTEM) (Tecnai G2 F20 U-TWIN field emission).

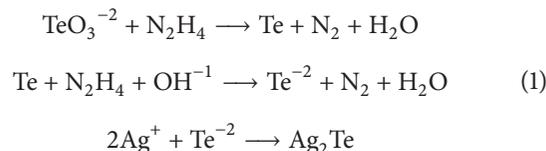
## 3. Result and Discussion

**$\text{Ag}_2\text{Te}$  Zigzag Nanostructures.** The first synthesis process which involves the production of silver telluride zigzag nanostructures was examined with the help of SEM reported

in Figure 1(a). Numerous long wiggly nanowires of diameter 50–60 nm and typical length of several tens of nanometers are formed. A detailed investigation was carried out using TEM and HRTEM. Figure 1(b) shows a distinctive low magnification TEM image of the zigzag nanostructure with the length of several micrometers. The inset of Figure 1(b) expresses the edge morphology of a typical zigzag nanowire.

EDS analysis (Figure 1(c)) generated with an electron nanoprobe is used to check the composition of nanowires. Spectrum shows that the product consists of Ag and Te elements at an atomic ratio close to the silver telluride stoichiometry, indicating the formation of  $\text{Ag}_2\text{Te}$  nanowires. The high resolution TEM and FFT images of representative nanowire are presented in Figure 2. The lattice fringes with 0.160 nm and 0.185 nm separations are normal for the (–501) and (004) plane d-spacing in monoclinic silver telluride structure. FFT pattern analysis demonstrates that the nanostructure exhibits the polycrystalline nature due to the ring pattern. The great change in volume can produce a rapid increment in stress in all directions, which leads to the multicrystalline nature.

These experimental results and previous reports [5, 7, 8] manifest that initially Te cluster form was obtained by the reduction of  $\text{Na}_2\text{TeO}_3$  in the presence of  $\text{N}_2\text{H}_4$ . Chemical reactions for this possible hydrothermal mechanism for the formation of silver telluride zigzag nanowires are as follows:



Since the shape of nanocrystals in synthesis relies on the surface energies of different facets that decrease when passivated by the capping agent, the affinity of the molecules of this agent is an essential parameter in finding out the nanostructure shape. Hence, in this whole process the most important role is of water soluble surfactant or stabilizing agent PVP. Its molecules are successfully employed as the structure directing agent for the growth of the zigzag morphology. Thus, we can speculate that existence of PVP in the reaction system has an effective influence on the crystal growth behaviour. The previous precursory researches have proposed that atoms on the different crystallographic facets have different interaction strength with a polymeric capping agent, leading to the anisotropic growth of a solid material [9–12]. Hence, the more plausible synthesis route is uninterrupted anisotropic growth along with the anisotropic surface passivation by the weak surfactant molecules resulting in the saw tooth-like surface along the growth axis.

**$\text{Ag}_2\text{Te}/\text{C}$  Core-Shell Structure.** A general overview of SEM picture shown in Figure 3(a) represents that the product obtained after the hydrothermal process at  $180^\circ\text{C}$  for 18 hrs is composed of nanowires ca. 100 nm and hundreds of micrometers in length.

In the high resolution TEM image (Figure 3(b)) there is an observable contrast between the inner core and external shell which suggests the core-shell structure. The heavy

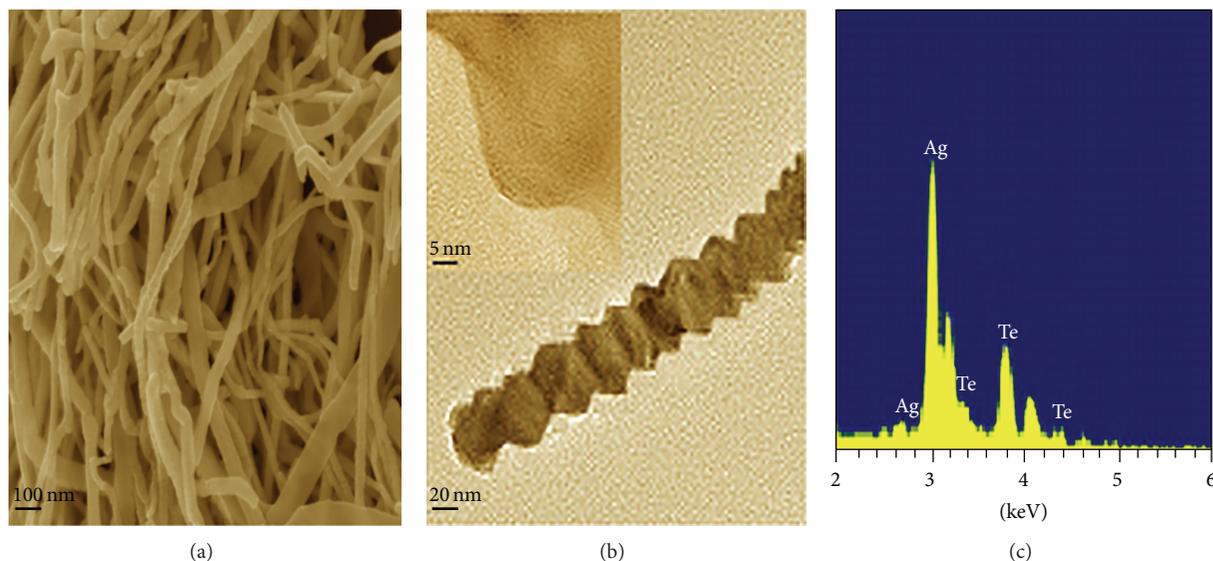


FIGURE 1: (a-b) The SEM and TEM images of fully grown zigzag  $\text{Ag}_2\text{Te}$ /nanowires; inset of (b) shows the morphology of the edge of the nanowire. (c) EDS spectrum of zigzag silver telluride nanowires.

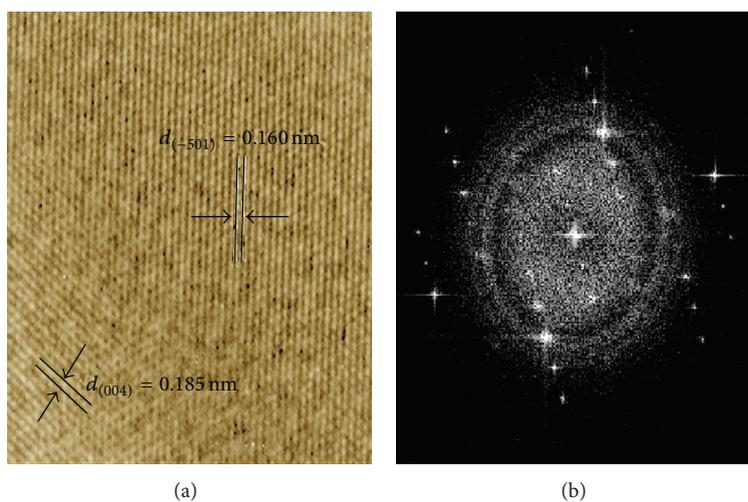


FIGURE 2: (a-b) The HRTEM image of a representative zigzag nanowire and its corresponding FFT ED pattern.

carbon coating has a consistent thickness of ca. 75 nm over the complete surface of inner silver telluride nanowire including the outer end also. Final, the EDS analysis shown in Figure 3(c) indicates strong Ag, Te, and C peaks, while the Cu peak originates from the supporting TEM grid. The amorphous carbon shell in completely grown nanostructure covering the edge can be clearly seen in Figure 4(a). This outer sheath effectively protects the inner metal telluride nanowires against attack from moisture and oxygen. The lattice spacing in HRTEM image of the inner core in Figure 4(b) is estimated to be 1.77 nm, which lies for (142) plane for monoclinic silver telluride.

The formation of the core-shell nanostructures continues under hydrothermal conditions which is greater than the normal glycosidation temperature and extends to aromatization and carbonization process [13]. This is in fact the

simplified view as there are a number of various chemical reactions of glucose which can occur under hydrothermal conditions in the sealed autoclave. In this synthesis process, reduction and carbonization route is followed by using the  $\text{Na}_2\text{TeO}_3$ ,  $\text{AgNO}_3$ , and the glucose as Te, Ag, and C sources, respectively. Ethylene glycol (EG) used here acts as reducing agent and provides the free cations  $\text{Ag}^{+2}$  and anions  $\text{TeO}_3^{-2}$  in the solution, and further reduction of  $\text{TeO}_3^{-2}$  to the elemental tellurium takes place very rapidly [14].

The reports [15–18] predict that in the hydrothermal process the nanowires grow first, and the carbon shell occurs as the last step. Thus, as the process continues, glucose in the system carbonises to amorphous carbon and an amorphous carbon coats on telluride nanowires surface and finally results in the formation of silver telluride core-shell nanostructure. Figure 5 presents the schematic view of the reaction sequence

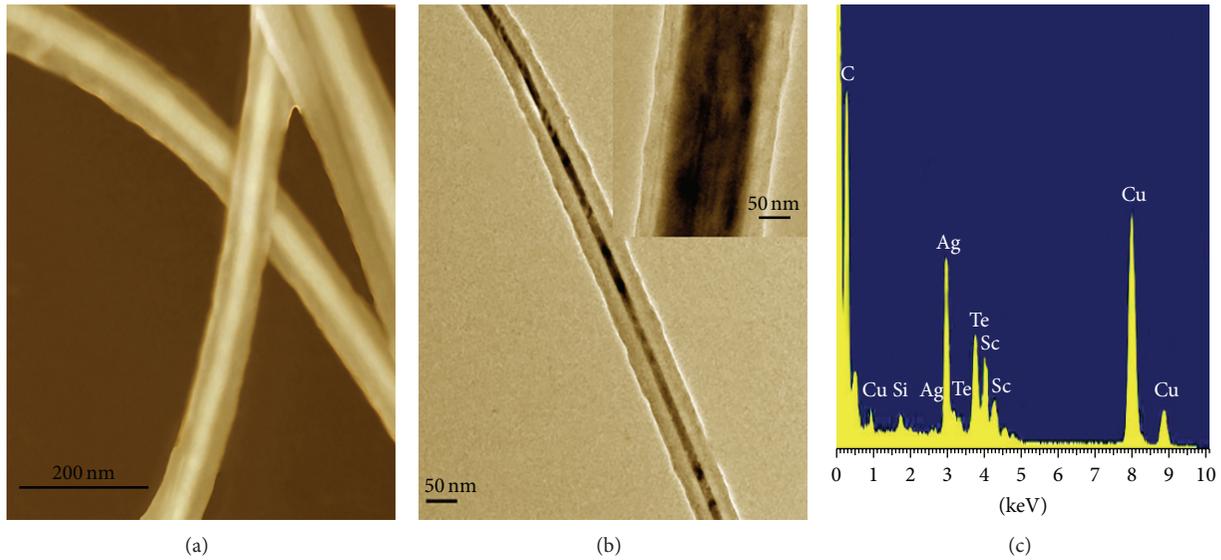


FIGURE 3: Magnified SEM and TEM images obtained from the presence of glucose at 180°C for 18 hrs. (a) A magnified SEM image of the nanowires. (b) and inset are the TEM images of the Carbon coated nanowires. (c) EDS spectrum of  $\text{Ag}_2\text{Te}/\text{C}$  nanowires.

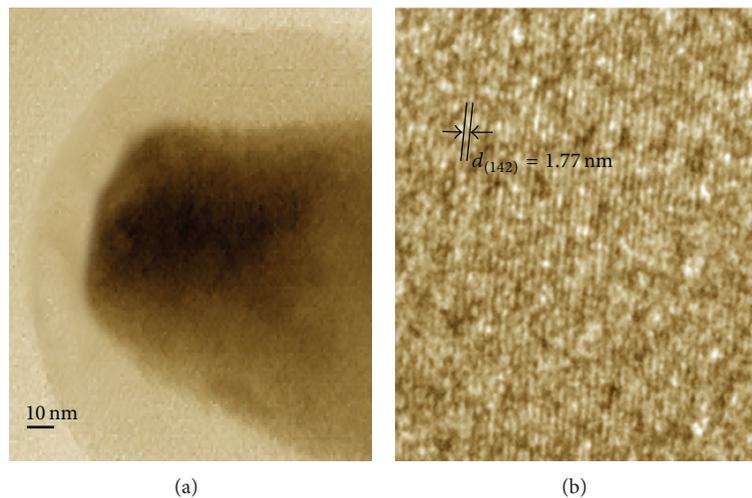


FIGURE 4: (a) TEM image of the edge of the fully grown  $\text{Ag}_2\text{Te}/\text{C}$  core-shell nanowires. (b) HRTEM image of the core of the nanowire.

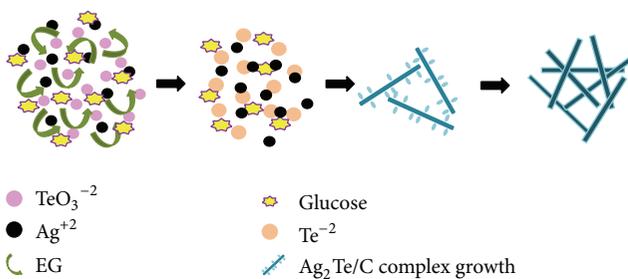


FIGURE 5: Schematic illustration of formation process of  $\text{Ag}_2\text{Te}/\text{C}$  nanowires.

of the growth of  $\text{Ag}_2\text{Te}/\text{C}$  nanowires. Briefly sodium tellurite and silver nitrate (precursors) dissolved in water are

converted to tellurite  $\text{TeO}_3^{-2}$  and  $\text{Ag}^{+2}$  ions in the presence of EG. In step (ii) the tellurite ions are rapidly converted to  $\text{Te}^{-2}$ . It should be noted that the glucose does not react in these reaction processes. When the temperature of the system increases the polymerization and carbonization reactions of glucose will take place, which finally produces the carbonaceous layer on the silver telluride nanowires [15].

#### 4. Conclusion

In summary, surfactant and carbonizing agent assisted morphology is presented for the silver telluride-based nanostructures. Unconventional zigzag silver telluride nanowires and silver telluride coated with carbon core-shell nanowires were synthesized via simple hydrothermal route. SEM, TEM, and EDS have been used to study the morphology and

composition. Unusual silver telluride nanowires here report the sawtooth-like zigzag nanowires in the presence of PVP. A growth model depicting the growth of core-shell nanowires via reduction-carbonization route is proposed. These unique structural characteristics of both morphologies can be evaluated by dispersing them in ethanol solution to excel their properties in viewpoint of applications in optoelectronic devices.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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