

# Shape-controlled synthesis and growth mechanism of one-dimensional nanostructures of trigonal tellurium

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Single crystalline one-dimensional (1D) nanostructures of trigonal tellurium (*t*-Te) with well-controlled shapes and sizes were synthesized by the hydrothermal reduction of Na<sub>2</sub>TeO<sub>3</sub> in a mixed solution of ethanol and water at 100 °C. The formation of various 1D nanostructures of *t*-Te was mainly determined by properly controlling the nucleation and growth rate of *t*-Te in different reaction media. In acidic solution (1 M of HCl), the reaction gave nanowires with diameters of ~30–100 nm, while in alkaline solution (1 M of NaOH), it yielded tubular crystals with diameters of ~1–2 μm. The diameters of tubular crystals could also be controlled by adjusting the NaOH concentration. When polymer surfactant poly(vinyl pyrrolidone) (PVP) was presented in the alkaline solution, the reaction would produce uniform nanowires with diameters of ~25 nm. Based on the TEM and SEM studies, the formation mechanisms for these 1D nanostructures were rationally interpreted. The crystallinity of the nanowires and the tubular crystals were determined by HRTEM, ED, and XRD.

## Introduction

The fabrication of one-dimensional (1D) nanoscale building blocks has been the subject of especially intense research because of the promising applications of these materials in various fields of nanotechnology, which also provide an ideal model system to experimentally investigate physical phenomena such as quantized conductance and size effects.<sup>1</sup> The size and shape of 1D nanostructures are two crucial factors in determining the properties of nanomaterials and thus, the control of size and shape is of great interest.<sup>2</sup> However, the synthesis of 1D nanomaterials is a challenge owing to their extremely small size and their anisotropic structures. Nowadays, the solution-phase approach has become a promising technique to preparing 1D nanostructures due to the relatively low cost and potential for large-scale production.<sup>3</sup> During the nanoparticles synthesis in solution phases, the control of nucleation and successive growth, which are extremely sensitive to the synthetic parameters, has been believed to be the key to the size- and shape-controlled synthesis of 1D nanostructures.<sup>4</sup> In some of the solution-phase synthesis routes, controlling size and shape of 1D nanostructure has been most successfully achieved by the use of either soft templates or structure-directing agents, including surfactants or polymers.<sup>5</sup> In addition, a seed-mediated growth approach has also been developed for the control of size and shape of 1D nanostructures in which the seeds are added to the synthetic system or formed *in situ* through a homogenous process.<sup>6</sup>

Trigonal tellurium (*t*-Te) and related materials have attracted more and more attention. Tellurium has a highly anisotropic crystal structure consisting of helical chains of covalently bond atoms, which are in turn bound together through van der Waals interactions into a hexagonal lattice.<sup>7</sup> As a semiconductor, tellurium exhibits a wealth of unique, useful

properties, such as photoconductivity, nonlinear optical responses, thermoelectric, or an effect of ultrafast electronic excitation on the *A*<sub>1</sub> phonon frequency, which result in their potential applications in electronic and optical electronic devices.<sup>8</sup> The availability of 1D nanostructures of tellurium should be able to bring in new types of applications or to enhance the performance of the currently existing devices as a result of quantum-sized effects. To date, the synthesis of 1D nanostructures of *t*-Te mainly depends on the solution-phase procedure.<sup>9–12</sup> Xia's group have reported the synthesis of various 1D nanostructures (wires, rods, and tubes) of *t*-Te through the reduction of orthotelluric acid (or tellurium oxide) in different solvent systems (ethylene glycol, water, and their mixtures) *via* a refluxing process.<sup>9,10</sup> In the earlier work of our group,<sup>11</sup> Te nanobelts and nanotubes were synthesized by the *in situ* disproportionation of Na<sub>2</sub>TeO<sub>3</sub> in an aqueous ammonia system under hydrothermal conditions. However, the conditions for the synthesis of nanobelts and nanotubes were quite restrictive. For example, the optimal pH for the synthesis was in a very narrow range of 12–12.5, and the synthesis needed a relatively high processing temperature (180 °C) and a relatively low concentration of the Na<sub>2</sub>TeO<sub>3</sub> (10 mM). Moreover, the as-synthesized products were usually a mixture of nanobelts and nanotubes as well as nanorods. This would lead to impurity of the products and a relatively small-scale synthesis.

In the present work, we present a facile and flexible hydrothermal reduction approach to the large-scale synthesis of 1D nanostructure of *t*-Te with well-controlled shapes and sizes. These highly anisotropic nanostructures are formed through the reduction of Na<sub>2</sub>TeO<sub>3</sub> by hydrazine in a mixture of ethanol and water at a low processing temperature (100 °C). Running the reaction in different media, such as acidic and alkaline solutions, or in the presence of surfactant poly(vinyl

pyrrolidone) (PVP), can give the products with various shapes and sizes. The present procedure also demonstrates a significant example for the shape- and size-controlled synthesis of nanostructures by properly adjusting reaction conditions.

## Experimental

### Synthesis

All of the chemical reagents used in these experiments were of analytical grade, and were purchased from Shanghai Chemical Reagents Company. The preparations of 1D nanostructures of *t*-Te were performed in different reaction media.

**(1) In acidic media.** A certain amount of  $\text{Na}_2\text{TeO}_3$  and HCl was dissolved into a mixture of 25 ml of ethanol and 25 ml of distilled water to give a solution containing 25 mM of  $\text{Na}_2\text{TeO}_3$  and 1 M of HCl. Subsequently, 0.5 ml of hydrazine monohydrate (~85%) was added into this solution. Then the resulting solution was transferred into a Teflon-lined autoclave of 60 ml capacity. The autoclave was maintained at 100 °C for 12 h and then cooled to room temperature naturally. The resulting solid products were filtered and washed, and finally dried in a vacuum at 60 °C for 4 h.

**(2) In alkaline media.** This procedure was similar to the above procedure except that NaOH was used instead of HCl.

**(3) In alkaline solution and in the presence of PVP.** 0.2 g of PVP (K30, polymerization degree 360) was added into the reaction mixture for procedure (2), and the period of the reaction time was elongated from 12 h to 48 h.

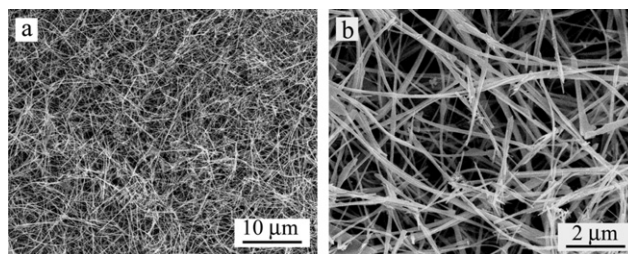
### Characterization

The X-ray diffraction (XRD) analysis was performed using a Rigaku (Japan) D/max- $\gamma$ A X-ray diffractometer equipped with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The SEM images were taken on a field emission scanning electron microscope (JEOL JSM-6300F, 15 kV). The TEM images were recorded on a Hitachi 800 transmission electron microscope (TEM) performed at 200 kV. The HRTEM images and the corresponding electron diffraction (ED) patterns were taken on a JEOL 2010 high-resolution transmission electron microscope performed at an acceleration voltage of 200 kV.

## Results and discussion

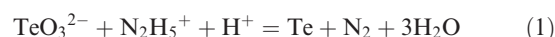
### Effect of the nature of the reaction media

We found that the products obtained in different reaction media were distinctly different in their shapes. In the acidic solution with 1 M HCl, the reaction gave a large amount of black fluffy solid that floated on the top of the reaction vessel. SEM images (Fig. 1a and 1b) demonstrate that the sample consists of a bulk of nanowires with the relatively uniform diameter of 30–100 nm and a typical length of tens of micrometers. When the reaction was processed in alkaline solution with 1 M NaOH, it produced a large quantity of needle-like crystals. Shown in Fig. 2a is the SEM image of this sample, indicating these needle-like crystals are usually 1–2  $\mu\text{m}$  in diameter and several hundred micrometers in length. Closer inspection demonstrates that they all have tubular structures. Some tubes with diameters as small as 100 nm can also be observed. Fig. 2b gives a magnified view of one of the tubular crystals, revealing that it consists of tubular hexagonal prisms, *ca.* 2  $\mu\text{m}$  in diameter and *ca.* 500 nm in thickness.

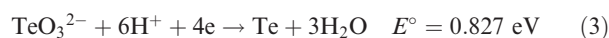


**Fig. 1** FESEM images of tellurium nanowires prepared in acidic solution with 1 M HCl. (a) Low-magnification view. (b) High-magnification view.

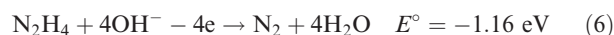
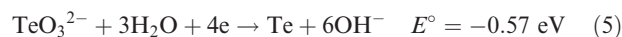
Obviously, the nature of the reaction media is the only factor that determines the shapes of the products. The reduction reaction in acidic and alkaline solution could be formulated as the following two equations, respectively.<sup>13</sup>



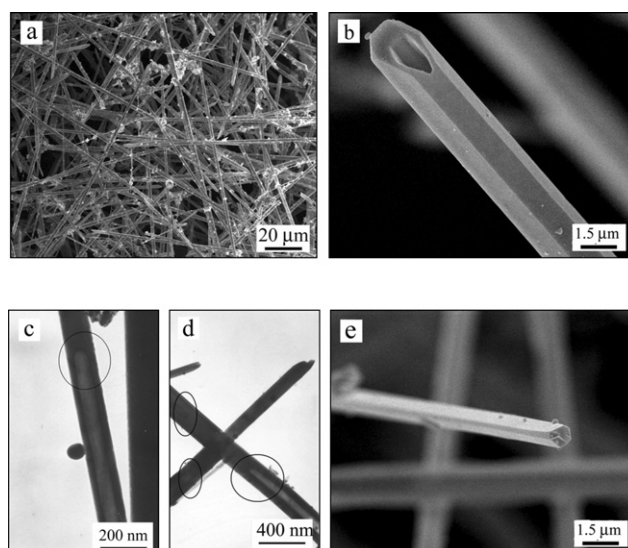
In acidic solution, the reaction comprises two half reactions



while in alkaline solution, they are



On the basis of the values of  $E^\circ$ , the standard electromotive force (EMF) of eqn. (1) and eqn. (2) could be estimated to be about 1.057 eV and 0.59 eV, respectively. This implied that the reduction reaction would be processed much more rapidly in acidic media than in alkaline media. In fact, the reduction in the 1 M of HCl solution was extremely rapid even at room temperature, and the reaction mixture quickly changed from clear to brown and finally to black within the first minute of the reaction. While in 1 M of NaOH solution, no precipitation



**Fig. 2** (a) FESEM images of tubular crystals of tellurium prepared in alkaline solution with 1 M NaOH. (b) FESEM image of a single tubular crystal, showing a tubular hexagonal prism. (c) and (d) TEM images of some tubular crystals with diameters in the range of ~100–200 nm, showing a distinct block region in the middle of each tube. The regions circled exhibit interface between the block region and the hollow region of the tube. (e) FESEM image of a typical rod-like crystal with a hexagonal prism.

was observed even after hydrothermal treatment at 100 °C for 2 h.

We believe that the nucleation and growth of tellurium nanowires in acidic media followed a mechanism similar to the previously reported one for the formation of selenium nanowires and tellurium nanowires.<sup>9,14</sup> The initial product of the reaction was amorphous tellurium (*a*-Te) colloids. When this mixture was aged under the present hydrothermal conditions, a small amount of *a*-Te would dissolve in the solution precipitated out as nanocrystallites of *t*-Te, and the *a*-Te colloids would slowly dissolve into the solution due to their higher free energies as compared to the seeds of *t*-Te. This dissolved Te subsequently grew as nanowires on the seeds of *t*-Te.

The nucleation and growth of tubular crystals in alkaline media seemed to follow a different mechanism. To clarify the formation mechanism of the tubular structures, we have investigated some tubular crystals with diameters in the range of 100–200 nm using TEM technique. Interestingly, the TEM images (Fig. 2c and 2d) show that there always is a distinct block region in the middle of each tube (see the circular ring regions in the two images). This suggests that the growth mechanism for the tubular structures should be similar to that for the Te nanotubes that were formed by adding orthotelluric acid to pure ethylene glycol refluxed at 197 °C.<sup>10</sup> When the reduction reaction was processed in the alkaline solution at 100 °C, it directly gave *t*-Te crystals instead of *a*-Te colloids owing to the very slow rate of the nucleation. These crystals would rapidly grow into rod-like crystals along the *c*-axis due to their highly anisotropic crystal structure. Fig. 2e shows a typical rod-like crystal with hexagonal prisms. Since the reduction reaction in alkaline media processed very slowly, it could not provide enough tellurium atoms for the growth of the growing rod-like crystals. This would lead to undersaturation in the central part of the growing faces of each seed (rod-like crystals), and the continuous addition of tellurium atoms to the seeds surface would preferentially occur at the circumferential edges of each regular-shaped seed because these sites had relatively higher free energies than other sites on the surface. Thus, the tubular structures would be formed because of no mass transportation to the inner region, and ‘two tubes’ could be grown on each seed at almost the same rate with opposite direction until all tellurium had been completely consumed, eventually resulting in the formation of tubular crystals having well-defined hollow interiors. We therefore assumed that both the sizes of the seeds (rod-like particles) and the successive growth of tubular crystals were mainly determined by the concentration of the NaOH that controlled reaction rate. Based on eqn. (2), the reaction rate would increase with a decrease of the concentration of NaOH. In fact, we found that the mean diameters of the tubular crystals increased from 0.5  $\mu\text{m}$  to 5  $\mu\text{m}$  with the concentration of NaOH increasing from 0.1 M to 2.5 M respectively. The formation of seeds with larger dimensions in a higher concentration of NaOH solution could be responsible for the growth of the tubular crystals with greater diameters. At 0.1 M of NaOH solution, however, the reaction gave a small fraction of rod-like crystals besides

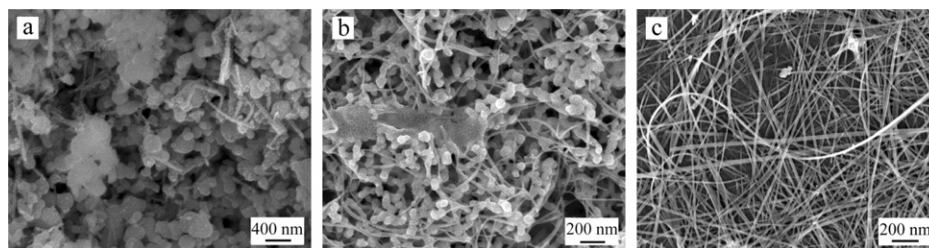
tubular crystals. As the concentration of NaOH decreased to 0.01 M, the product mainly consisted of rod-like crystals. These results confirmed that the rod-like particles could not develop into the tubular structures when the reaction could provide enough tellurium atoms for the growth of these rods.

Furthermore, the ethanol also played an important role on the formation of the tubular structures. In the case of pure water, the formation of pure tubular crystals needed a higher concentration of NaOH in pure water than in the mixture of ethanol and water as solvent. This was because the solubility of tellurium was greater in ethanol than in water under solvothermal condition.<sup>15</sup> Such a behavior was in agreement with the previous report that the tubular selenium and tellurium crystals could be formed in suitable solvents in which the solid had an appropriate solubility.<sup>15</sup>

### Effect of the surfactant PVP

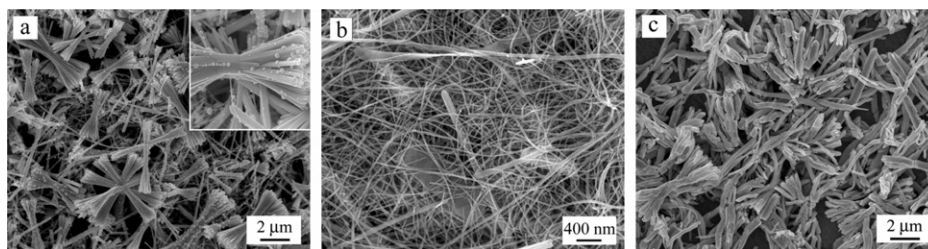
Recently, the polymer surfactant PVP has been successfully employed as stabilizing agent as well as structure-directing agent for the preparation of silver nanoparticles (including nanowires).<sup>16</sup> PVP played an important role on the control of the nucleation and growth of silver nanowires through the selective adsorption on the facets of the growing particles. In this work, PVP was also introduced to the synthetic system. Fig. 3a–c shows the SEM images of three samples that were prepared by running procedure (3) at different periods of reaction time after the onset of reaction. A comparison between these images clearly reveals the formation of colloids as uniform spheres ( $\sim 100$  nm in size) instead of tubular crystals after aging for 12 h. As shown in Fig. 3b, the sample prepared after aging for 24 h contained a notable presence of uniform nanowires with diameters of  $\sim 25$  nm. Fig. 3b also indicates that the spherical particles were still present in the solution after a growth period of 24 h. After 48 h, the product consisted of pure nanowires with uniform diameters of 20–30 nm and lengths greater than 10  $\mu\text{m}$ . It could be believed that such a process of nanowire growth should ascribe to the presence of the polymer surfactant PVP. Because PVP strongly adsorbed on the surface of the initial formed tellurium particles was an obstacle to tellurium diffusion, the product obtained after aging for 12 h was *a*-Te colloids that consisted of the spherical particles. As the colloids were aged at 100 °C, both the nucleation of *t*-Te and the growth of nanowires proceeded in a relatively low rate. Nevertheless, these processes were similar to these for the above-mentioned nanowires formed in the acidic media. But the seeds (*t*-Te) were very uniform and small and thus, they would lead to the formation of uniform nanowires with smaller diameters as shown in Fig. 3c. The generation of small seeds should be attributed to the selective adsorption of PVP molecules on some different crystalline planes of *t*-Te. Such adsorption could significantly decrease the growth rate of these planes and also lead to a highly anisotropic growth.

It is well known that the surfactant PVP has a great effect on preventing the nanoparticles from aggregating and, such an effect of the antiagglomeration could largely depend on the



**Fig. 3** FESEM images of three samples prepared in 1 M of NaOH aqueous solution and with the addition of 0.1 g of PVP, showing the morphology evolution of the tellurium nanowires. These samples were taken after the reaction had proceeded for (a) 12 h, (b) 24 h, and (c) 48 h, respectively.





**Fig. 4** FESEM images of the samples prepared by varying the quantity of the PVP or the temperature: (a) 0.01 g of PVP, at 100 °C for 48 h; (b) 0.05 g of PVP, at 100 °C for 48 h; and (c) 0.1 g of PVP, at 125 °C for 48 h. All the reactions were processed in alkaline solution with 1 M of NaOH.

steric effect arising from the long polyvinyl chain of PVP on the surface of the growing particles.<sup>16</sup> Because the steric effect was largely determined by the covered fraction of PVP on the surface of the particles, the quantity of PVP, therefore, should be an important factor in determining both the shape and the size of the final product. When even a very small amount of PVP (0.01 g) was added, the reaction gave a product with distinctly different shape from the tubular structures obtained in the absence of PVP. As shown in Fig. 4a, the product was a mixture of bow-like microcrystals (~80% of the total particles) and nanowires. These bows showed an interesting structure with branched bundles. Each of them grew three-dimensionally, not in a plane, in the opposite direction from its center, and the element rods of the bow had diameters of ~50–100 nm and lengths of ~2 μm. This suggested that seeds with dimensions of several hundred nanometers would be formed firstly, but they could not develop into tubular structures because of the protective effect of PVP. Furthermore, second nucleation would occur on the surfaces (usually  $\pm(001)$  planes) of these seeds due to lack of enough of PVP to coat the growing particles. When the amount of the PVP was increased to 0.05 g, the products mainly consisted of nanowires with diameter of ~20–30 nm (Fig. 4b), indicating that increasing the amount of PVP in the reaction mixture leads to decreased sizes of seeds.

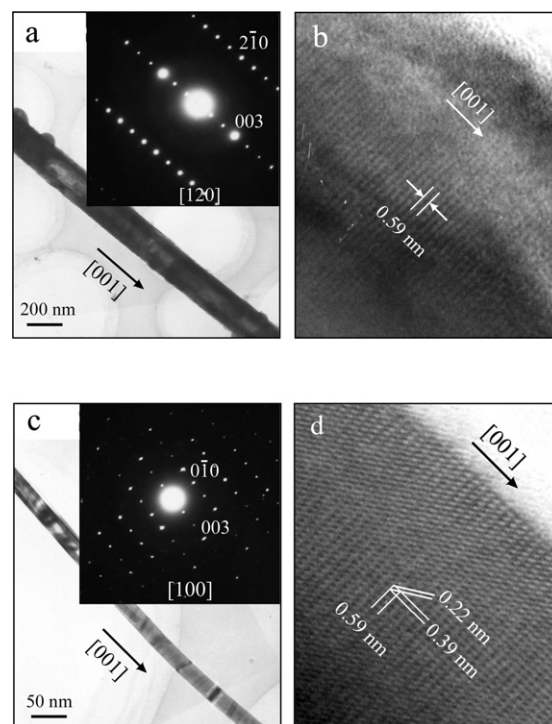
Additionally, we found the reaction temperature was also a crucial factor for the formation of nanowires. At 125 °C, the reaction also gave bow-like crystals, but they had very irregular surfaces and their branches had large diameters of ~200 nm (see Fig. 4c). This is because the steric effect of PVP may be decreased with increasing temperature.

### Structural characterization of tubes and nanowires

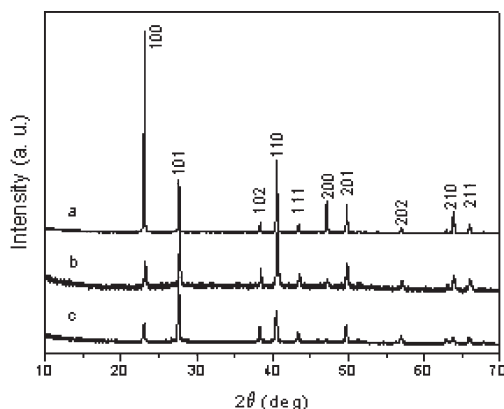
We investigated the structure of *t*-Te tubes and nanowires in more detail with ED and HRTEM. A typical tubular crystal with diameter of ~200 nm (Fig. 5a) was properly chosen as the object for the investigation. The HRTEM image in Fig. 5b shows a lattice spacing (*ca.* 0.59 nm) that agrees with the separation between the (001) planes of *t*-Te. The inset of Fig. 5a shows the corresponding ED pattern of the tubes, which was obtained by focusing the electron beam along the [120] zone axis of an individual tube. The HRTEM image and ED pattern both demonstrated that the tubular crystal was single-crystalline and grew along the [001] direction. Shown in Fig. 5c is the TEM image of an individual nanowire with a diameter of *ca.* 25 nm, which was prepared in alkaline media and in the presence of PVP, indicating the uniformity in diameter along the entire longitude. The inset ED pattern of the nanowire shown in Fig. 5c was recorded with the electron beam along the [100] zone axis. It demonstrated that this nanowire was a single crystal with a growth direction of [001]. An HRTEM image (Fig. 5d) taken from the wire as in Fig. 5c shows three set of distinct lattice spacings of *ca.* 0.59, 0.39, and 0.22 nm that correspond to the (001), (010), and (011) planes of *t*-Te, respectively. This HRTEM image further confirmed the single-crystal nanowire grew along the [001] direction. It also shown that the nanowire was structurally

uniform and no dislocation or other planar defects were observed in the examined area of this nanowire. From the above results, it could be concluded that the *t*-Te crystals had a strong tendency to grow along the [001] direction, with the helical chains of tellurium atoms parallel to the longitudinal axis. This predominantly attributed to its highly anisotropic structure.

The crystallinity and purity of these tubes and nanowires were also studied by XRD. Fig. 6a, 6b and 6c show the typical XRD pattern for tubular crystals, nanowires prepared in acidic media, and nanowires prepared in alkaline solution, respectively. All the diffraction peaks in these patterns can be indexed to the trigonal phase of tellurium. The relative intensity of the peaks in Fig. 6b and 6c agrees well with that in the JCPDS card (no. 36-1452). Compared to Fig. 6b and 6c, Fig. 6a exhibits an abnormal intensity of the 100 and 110 peak. This indicates that these tellurium tubes had been preferentially grown along the [001] direction, and their hexagonal prisms were terminated with four {100} and two {110} planes. The preferred prismatic surfaces for the hexagonal tubular structures could be responsible for the relatively low surface free energy values of the {100} and {110} planes compared to these of other planes.<sup>17</sup>



**Fig. 5** (a) TEM image of a single tellurium tubular crystal. The inset is the ED pattern that was obtained by focusing the electron beam on the tube. (b) HRTEM image taken from the edge of the tube. (c) TEM image and ED pattern (inset) of an individual nanowire that was taken from the sample shown in Fig. 3c. (d) HRTEM image obtained from the edge of the nanowire shown in Fig. 5c.



**Fig. 6** The XRD patterns of the products. (a) The tubular crystals prepared in alkaline solution. (b) The nanowires with diameters of ~30–100 nm obtained in acidic solution. (c) The nanowires with diameters of ~25 nm obtained in 1 M of NaOH solution and in the presence of 0.1 g of PVP.

## Conclusion

In summary, single crystalline 1D nanostructures of *t*-Te with well-controlled shapes and sizes have been synthesized by running the hydrothermal reaction in different media. Tubular crystals and nanowires could be obtained in alkaline and acidic solution, respectively. The diameters of tubular crystals can be readily controlled by adjusting the NaOH concentration. With the assistance of PVP, the reaction produced bulk of nanowires with diameters of ~25 nm. In these soft processes, the formation of various 1D nanostructures of *t*-Te was mainly determined by controlling the nucleation and growth rate of *t*-Te indifferent reaction media. The as-prepared 1D nanostructures with various shapes and sizes might lead to various applications for *t*-Te.

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