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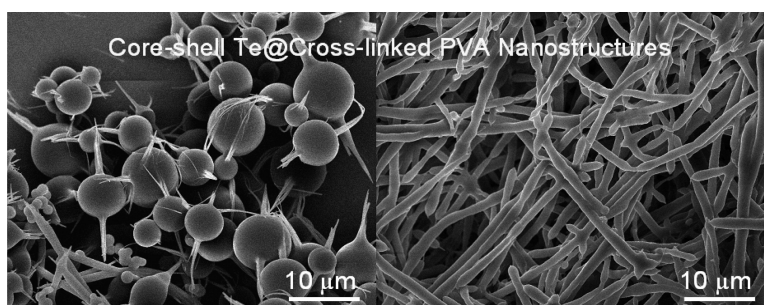
## Article

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# Te@Cross-Linked PVA Core–Shell Structures Synthesized by a One-Step Synergistic Soft–Hard Template Process

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**ABSTRACT:** Recently, we proposed a simple, large-scale hydrothermal synthesis of flexible nanocables with silver as cores and cross-linked poly(vinyl alcohol) (PVA) as shells in which silver ions catalyzed the cross-linking of PVA chains under hydrothermal conditions and a so-called synergistic soft–hard template mechanism (SSHM) was proposed (Luo et al. *J. Am. Chem. Soc.* **2005**, *127*, 2822–2823). In this paper, we extend this approach to examine whether high valent metal ions such as  $\text{Te}^{4+}$  also can be reduced under a similar reaction but using sodium tellurite and PVA as precursors. The results demonstrated that different tellurium/cross-linked PVA core–shell nanostructures such as a core–shell structure with nanorod bundles penetrated through a ball, branched cables, and separated cables can be synthesized. The influence of the concentration of PVA, reaction temperature, and reaction time on the formation of different nanostructures has been investigated. In addition, the detailed reaction and shape evolution process of core–shell structures have also been studied. The results suggested that the cross-linking of PVA also can occur in the presence of high valent metal ions besides noble metal ions, underlining that it is possible to access various core–shell structures with different inorganic components as cores by this approach.

## Introduction

Core–shell nanostructures have received intense attention due to their improved physical and chemical properties over their single-component counterparts, which are of great importance to a potentially broader range of applications in electronics, magnetism, optics, and catalysis.<sup>1</sup> Since the discovery of coaxial nanocables in 1997,<sup>2</sup> many techniques have been developed to fabricate various nanocables or core–shell nanostructures, for instance, laser ablation,<sup>2,3</sup> chemical vapor deposition and epitaxy,<sup>4</sup> electrophoretic deposition or electrochemical deposition,<sup>5</sup> carbothermal reduction methods,<sup>6</sup> and solution reaction or sol–gel process.<sup>7</sup> Most of these techniques need either hard templates such as carbon nanotubes, Ni nanorods, anodized aluminum oxide (AAO) templates or rigorous reaction conditions.

Searching for new synthetic strategies for the synthesis of core–shell nanostructures such as nanocables has been a hot topic due to their important potential applications in nanoscale electronic devices, cell separation, and medicine delivery.  $\gamma$ -Irradiation method has been adopted to synthesize a kind of hybrid nanocable with semiconductor wire in a polymer sheath (CdSe/poly (vinyl acetate)).<sup>8</sup> Recently, coaxial nanostructures based on single walled carbon nanotubes (SWNT) backbone and conducting shells of polypyrrole or polyaniline and  $\text{Fe}_2\text{O}_3$ @polystyrene core–shell nanoparticles have been reported by polymerization of the monomers on the surface of SWNT and  $\text{Fe}_2\text{O}_3$ , respectively.<sup>9</sup> More recently, we have developed a synergistic soft–hard template method to synthesize flexible Ag (or Cu)/cross-linked poly(vinyl alcohol) (PVA) coaxial nanocables<sup>10</sup> and Ag@carbon nanocables<sup>11</sup> under hydrothermal conditions. Ag/polypyrrole nanocables have been fabricated in aqueous solution through a redox reaction between silver nitrite and pyrrole in aqueous solution at room temperature with addition of poly (vinyl pyrrolidone) used as a coordinating agent.

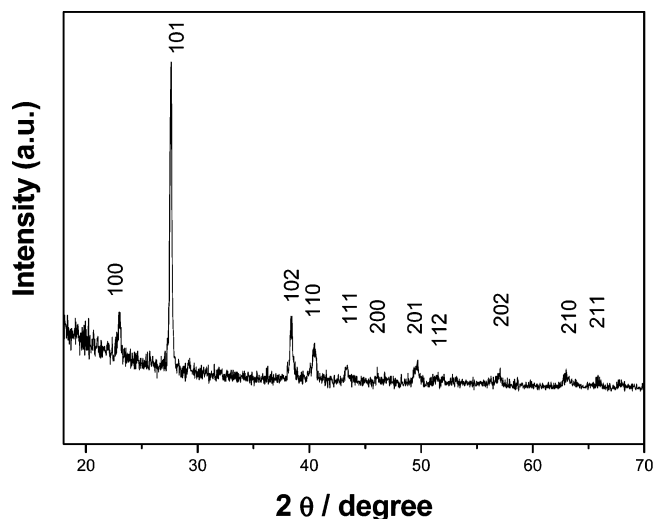
Tellurium as a narrow direct band gap (band gap energy of 0.35 eV) semiconducting material has attracted wide interest due to its interesting optical properties and potential use as a holographic recording material, an infrared photoconductive detector, and for nonlinear-infrared optics, such as second harmonic generation.<sup>12</sup> Tellurium has a highly anisotropic growth tendency to form one-dimensional nanostructures including nanobelts,<sup>13</sup> nanowires,<sup>14</sup> nanotubes,<sup>15</sup> and nanorods<sup>16</sup> because of its unique helical-chain conformation in its crystal structure.<sup>17</sup> Tellurium nanowires and nanotubes have been synthesized by distinct routes including a polyol process,<sup>18</sup> aqueous solution approach,<sup>19</sup> and solvothermal and hydrothermal approaches.<sup>20,21</sup> Recently, biomolecules such as aliginic acid amino acids have been used as additives for the synthesis of Te nanowires<sup>22</sup> and scrolled tellurium nanotubes.<sup>23</sup> To the best of our knowledge, there have been no reports on the synthesis of core shell nanostructures with Te as the core component and polymers as the shell component.

In this paper, a synergistic soft–hard template method under hydrothermal conditions<sup>10</sup> has been extended to synthesize different tellurium/cross-linked PVA core–shell nanostructures by controlling the amount of PVA and the reaction temperature. The concentration of PVA, reaction temperature, and reaction time play key roles in the formation of different nanostructures. The detailed reaction and shape evolution process of core–shell structures have been studied.

## Experimental Section

All chemicals were of analytical grade and were received from Shanghai Chemical Ltd Co. The chemicals were used without further purification. In a typical experimental process, 0.0553 g of sodium tellurite (0.25 mmol) was added into a 21 mL PVA (3 wt %) solution in a beaker and stirred vigorously and formed a clear solution. After that, the previous solution was transferred into a Teflon-lined stainless steel autoclave (27 mL in total volume), which was closed and maintained at 190 °C for 48 h in a digital temperature controlled oven, and then the sample was allowed to cool to room temperature naturally. The resulting sage green floccule was filtered and washed several times

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**Figure 1.** X-ray diffraction (XRD) pattern of as-prepared product obtained from reaction of 0.25 mmol of sodium tellurite with a 21 mL PVA solution (3% w/w) at 190 °C for 48 h.

with double distilled water and absolute ethanol and dried in a vacuum at 60 °C for 4 h.

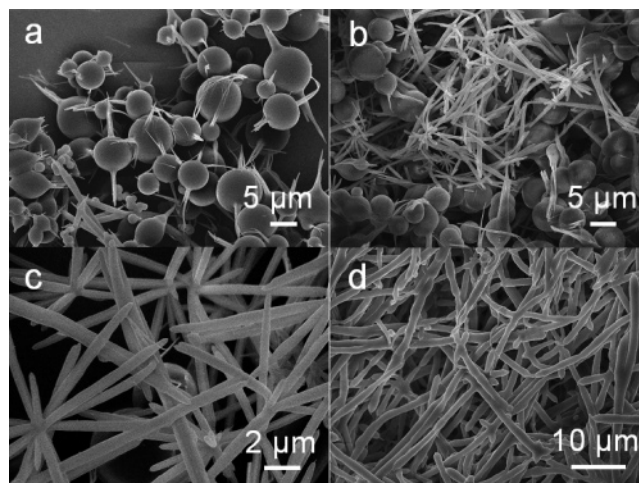
The final products were characterized by X-ray power diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS). XRD analyses were carried out on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å), and the operation voltage and current were maintained at 40 kV and 40 mA, respectively. TEM was performed on a Hitachi (Tokyo, Japan) H-800 transmission electron microscope at an accelerating voltage of 200 kV, and HRTEM (JEOL-2010) was operated at an acceleration voltage of 200 kV. The FTIR spectra of the samples were measured on a MAGNA-IR 750 at room temperature (Nicolet Instrument Co., U.S.A.).

## Results and Discussion

Figure 1 shows the XRD pattern of the as-prepared product obtained at 190 °C for 48 h; all peaks can be indexed as a hexagonal phase of tellurium (t-Te) with calculated cell constants  $a = 4.47$  Å and  $c = 5.89$  Å, which are in good agreement with the standard literature values (JCPDS, 36-1452,  $a = 4.457$  Å,  $c = 5.927$  Å), and no other impurity peaks were detected. SEM was used to observe the evolution of morphologies of the products obtained from the reaction of sodium tellurite with different amounts of PVA at 190 °C for 48 h, and the results are shown in Figure 2.

The amount of PVA plays a key role in the formation of various core-shell nanostructures of Te/cross-linked PVA. The corresponding TEM images of these samples are shown in Figure 3. When sodium tellurite (0.25 mmol) reacts with 5 mL of PVA (3% w/w), it cannot form core-shell nanostructures completely, and the resulting particles are in a form of ball-like core-shell structures with nanorod bundles penetrated through the ball (Figure 2a). A mixture of the ball-like core-shell structures with nanorod bundles penetrated through the balls, and nanocables formed if the amount of PVA was kept as 10 mL. If the amount of PVA is increased up to 15 mL, branched coaxial nanocables of ca. 1  $\mu$ m in diameter and several micrometers in length can be produced. In fact, the single coaxial nanocable consisted of nanowire bundles of tellurium (Figure 3c).

Upon further increasing the amount of PVA up to 21 mL, uniform and flexible nanocables of 400 nm to 2  $\mu$ m in diameter



**Figure 2.** The SEM images of the product synthesized by reaction of 0.25 mmol of sodium tellurite with different volumes of 3% PVA solution at 190 °C for 48 h (a) 5 mL, (b) 10 mL, (c) 15 mL, (d) 21 mL, respectively.

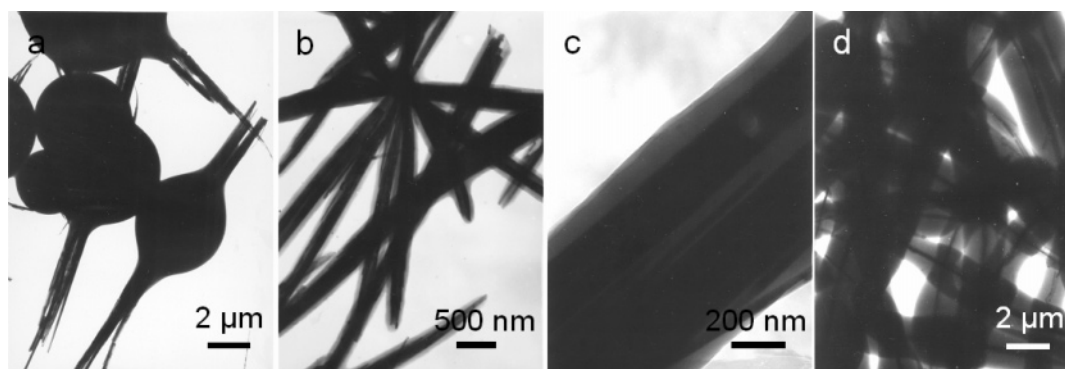
and tens of micrometers in length were produced (Figure 2d). Each cable consisted of a smooth core of about 50–70 nm in diameter and a surrounding sheath of about 0.2–1  $\mu$ m in thickness (Figure 3d). In general, tellurium has a highly anisotropic growth tendency due to its unique crystal structure. The typical single cable is shown in Figure 4a. The corresponding electron diffraction pattern taken on the single wire in its core clearly shows its single crystallinity. The high-resolution TEM image of tellurium nanowires taken on the tip of the nanocable shows that the fringes with a spacing of 0.59 nm, which is perpendicular to the axial direction, correspond to the interplanar distance of {001} planes. These results demonstrated that the core nanowires of tellurium grew along the [001] direction, which is in good agreement with previous reports.<sup>14</sup>

Moreover, for comparison, the reaction of Na<sub>2</sub>TeO<sub>3</sub> with PVA (1 mL or less) under similar hydrothermal conditions leads to the formation of tellurium nanorods and nanowires without core-shell nanostructures. In addition, the degree of cross-linked PVA is not high when more sodium tellurite (0.75 mmol) reacted with a 21 mL PVA (3% w/w) solution at 190 °C for 48 h, which is strongly dependent on the ratio of the reactants.

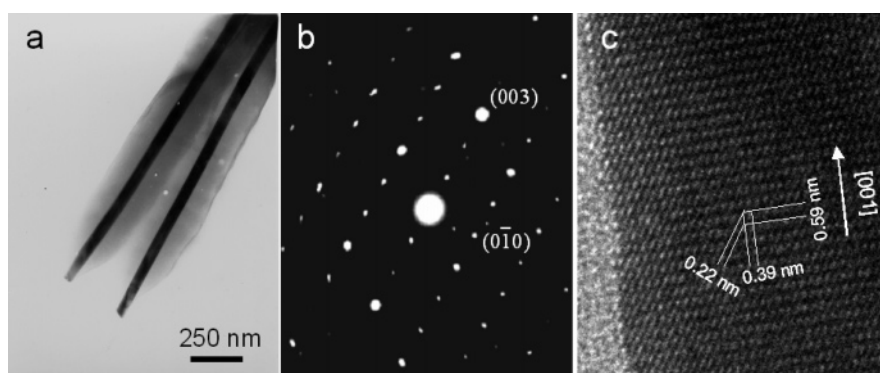
X-ray photoelectron spectra of the samples obtained under different conditions were obtained for the examination of the composition of the surface. Peak values at 284.82 and 532.96 eV can be assigned readily to the binding energies of C<sub>1s</sub> and O<sub>1s</sub>, respectively; the peaks with binding energies at 574.56 eV for Te<sub>3d5</sub> were very weak and could hardly be detected, indicating that all of the tellurium in these products are confined within the shells of cross-linked PVA (Figure 5).

The cross-linking reaction of PVA that occurred at a relatively low temperature in the presence of silver ions could be due to the closed hydrothermal reaction conditions.<sup>10</sup> Here, the temperature plays a critical role in the formation of core-shell nanostructures. Only tellurium nanowires without sheaths were obtained at 180 °C in large scale under similar hydrothermal conditions as shown in Figure 6, indicating that the cross-linking reaction of PVA has not occurred under the present conditions even at 180 °C, even though the temperature is higher than that of our previous results in the presence of silver ions.<sup>10</sup> Mo and co-workers have synthesized tellurium nanobelts and nanotubes successfully by the disproportionation reaction of sodium tellurite with no addition of polymer at 180 °C by a hydrothermal process,<sup>13a</sup> implying that the formation of tellurium nanowires

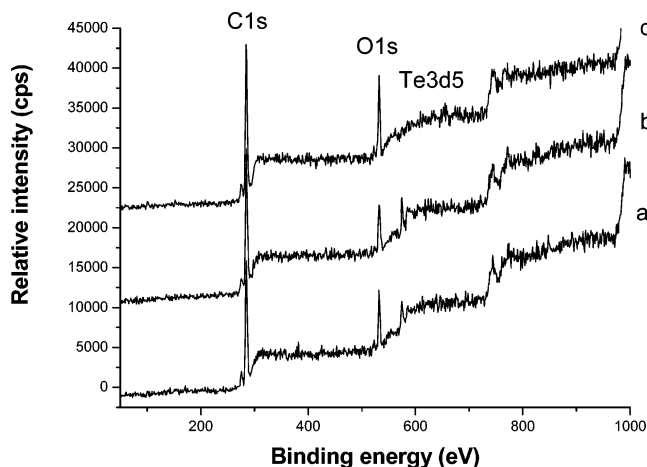




**Figure 3.** The TEM images of the as-prepared product obtained by reaction of 0.25 mmol of sodium tellurite with different volumes of 3% PVA solution at 190 °C for 48 h (a) 5 mL, (b–c) 15 mL, (d) 21 mL, respectively.



**Figure 4.** (a) Typical TEM image of the Te/cross-linked PVA nanocables. (b) Electron diffraction pattern taken on a single cable. (c) HRTEM image of the core nanowire. The sample was obtained by reaction of 0.25 mmol of sodium tellurite with a 21 mL 3% PVA solution at 190 °C for 48 h.

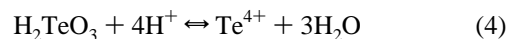
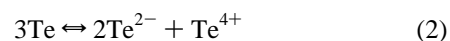
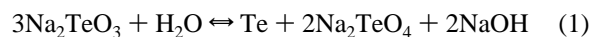


**Figure 5.** (a–c) XPS spectra of the samples with various core–shell nanostructures of tellurium/cross-linked PVA shown in Figure 2, panels a, c, and d, respectively. The products were synthesized by reaction of 0.25 mmol of sodium tellurite with different volumes of 3% PVA solution at 190 °C for 48 h: (a) 5 mL, (b) 15 mL, (c) 21 mL.

obtained at 180 °C is due to the disproportional reaction of sodium tellurite and that PVA only acts as a polymer surfactant or protecting agent. The pH value of the resulting solution increased from the starting initial solution of 8.2 to 9.8 at 180 °C, suggesting that PVA is not cross-linked under these conditions, in which PVA acted as a polymer surfactant or protecting agent as that has been widely used as a protecting agent to synthesize silver nanowires,<sup>24</sup> CdSe and CdTe nanowires,<sup>25</sup> etc. However, the pH value of the resulting solution dropped dramatically from the initial solution 8.0 to ca. 1.3 at

190 °C for 48 h, implying that the PVA cross-linked reaction occurred and released a lot of H<sup>+</sup> ions.

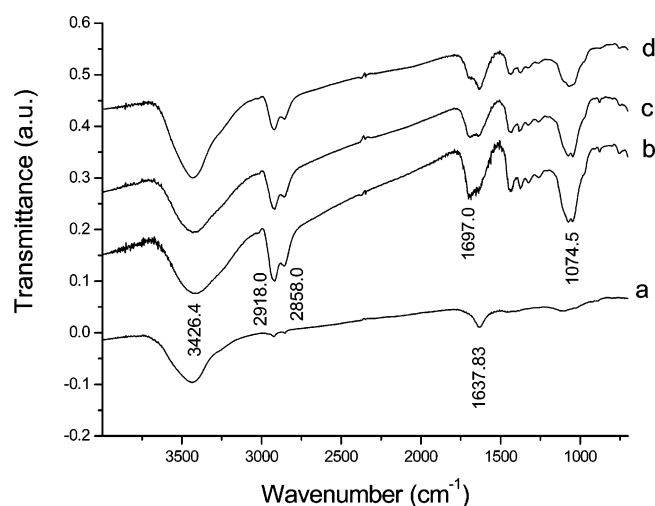
Recently, a self-sacrificing template process to synthesize Ag<sub>2</sub>-Te fibers by a disproportional process of Te<sup>0</sup> into Te<sup>2-</sup> and Te<sup>4+</sup> in the presence of silver ions was reported,<sup>26</sup> which is to some extent similar to that proposed in the case of Se.<sup>27</sup> On the basis of the above analysis and our previous results, there should be new species produced during the formation of various core–shell nanostructures of Te/cross-linked PVA. The reactions that occurred can be formulated as:



It is well-known that PVA contains three kinds of hydrogen atoms, i.e., hydrogens in hydroxy, methylidyne, and methylene. The cross-linking reaction of PVA demonstrated here is in fact a dehydrogen process (one hydrogen atom of hydroxyl and, at the same time, another hydrogen atom of methylidyne). As to the possible formation mechanism of the various Te/cross-linked nanostructures, it is to some extent similar to the so-called synergistic soft–hard template mechanism (SSHMTM),<sup>10</sup> which was proposed to explain the formation mechanism of elegant nanocables of Ag/cross-linked PVA. Here, we propose that Te<sup>4+</sup> is reduced by a hydrogen atom of methylidyne of PVA due to the strong interaction between Te<sup>4+</sup> and PVA, which leads to a



**Figure 6.** The TEM image of the product obtained by a hydrothermal process at 180 °C for 48 h.



**Figure 7.** The FT-IR spectra of (a) pure PVA; different Te/cross-linked PVA core-shell structures obtained from reaction of 0.25 mmol of sodium tellurite with different volumes of 3% PVA solution at 190 °C for 48 h: (b) 5 mL, (c) 15 mL, (d) 21 mL, respectively.

dehydrogen process and allows the PVA cross-linked reaction to form the nanocables.

PVA is also responsible for both reduction of  $\text{Te}^{4+}$  into Te and further oriented growth of tellurium nanowires stabilized

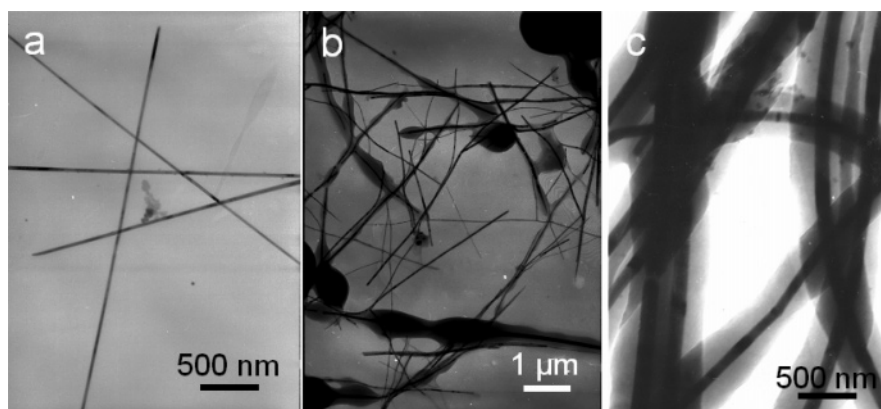
by PVA. Meantime, the cross-linking reaction of PVA occurs and forms on the newly formed tellurium nanowires. FT-IR spectra show that there is a wide absorption peak at  $1070\text{ cm}^{-1}$  in these samples (Figure 7), which can be assigned as the absorption peak of  $\sigma_{\text{as}}(\text{C}-\text{O}-\text{C})$  of the cross-linked PVA.<sup>10</sup> Compared with that for the pure PVA, there are more enhanced absorption peaks from 1050 to  $1100\text{ cm}^{-1}$  in the core-shell structures containing cross-linked PVA. The presence of a new absorption peak around  $1697.0\text{ cm}^{-1}$  suggested that some carbonylate exists and can be indexed to the  $\nu\text{C}=\text{O}$  as in  $\text{R}-\text{COOH}$ .

A time-dependent shape evolution process of cables was followed. The TEM images of morphological evolution of the products obtained after the reaction for different times are shown in Figure 8. Only tellurium nanowires formed in the initial stage of the reaction at 190 °C for 4 h (Figure 8a). The pH value of the resulting solution increased slightly from the initial pH value of 8.0 to 8.70, implying that the corresponding reaction in the initial stage can be illustrated as eq 1. Te/cross-linked PVA nanocables and tellurium nanowires also can be observed clearly after the reaction for 12 h (Figure 8b). With prolonged time, the cross-linked PVA is well wrapped around the nanowires to form cable-like structures (Figure 8c). The formation of various Te/cross-linked nanostructures can be attributed to the synergistic soft-hard template effects between  $\text{Te}^{4+}$  and PVA. It should be pointed out that the synergistic soft-hard template mechanism is not completely understood and needs to be studied further.

The schematic illustration of the formation process of the different nanostructures in the presence of different amounts of PVA is summarized in Scheme 1, showing that PVA has a special effect on the formation of these core-shell nanostructures. The formation of different core-shell nanostructures can be attributed to the two important roles of PVA in this process. PVA can be not only used as a protecting agent to direct the preferential growth of tellurium along the [001] direction and result into the formation  $\text{Te}@\text{cross-linked PVA}$  nanocables with tens of micrometers in length, but also it can be used as a reducing agent to reduce the precursor into tellurium and then start to cross-link on the surface of the newly formed tellurium nanostructures simultaneously.

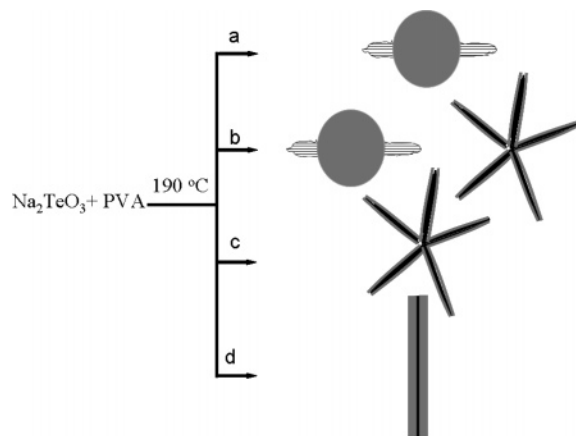
## Conclusions

In summary, a series of Te/cross-linked PVA core-shell structures with tellurium as cores and cross-linked PVA as shells have been prepared successfully in large scale by a reaction of sodium tellurite and PVA under suitable hydrothermal condi-



**Figure 8.** TEM images of as-prepared product obtained by reaction of 0.25 mmol of sodium tellurite with a 21 mL PVA (3%, w/w) solution at 190 °C for different reaction periods: (a) 5 h, (b) 12 h, (c) 24 h, respectively.

**Scheme 1. Illustration of the Formation of Different Te/Cross-Linked PVA Nanostructures Which Are Strongly Dependent on the Amount of PVA<sup>a</sup>**



<sup>a</sup> The reaction of 0.25 mmol of sodium tellurite with different amounts of 3% PVA solution at 190 °C for 48 h: (a) 5 mL, (b) 10 mL, (c) 15 mL, (d) 21 mL, respectively.

tions. Tellurium/cross-linked PVA core–shell nanostructures such as Te nanorods penetrated ball-like structures, branched core–shell structures, and well-defined nanocables can be synthesized based on a synergistic soft–hard template mechanism (SSHM). The concentration of PVA, the reaction temperature, and reaction time are crucial for the formation of different nanostructures. The results demonstrated that the so-called SSHM technique can be extended to synthesize other core–shell nanostructures including nanocables with different inorganic components as cores besides noble metals such as Ag and Cu.<sup>10</sup> These new forms of core–shell nanostructures could be of importance for the further study of their applications such as in nanoscale electronic devices, cell separation, drug delivery, and microreactors.

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