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## Preparation of Fluorescent Tellurium Nanowires at Room Temperature

Zong-Hong Lin,<sup>†</sup> Zusing Yang,<sup>†</sup> and Huan-Tsung Chang<sup>\*,†,‡</sup>

Department of Chemistry, National Taiwan University, Taipei, Taiwan and Department of Natural Science Education, National Taitung University, Taitung, Taiwan

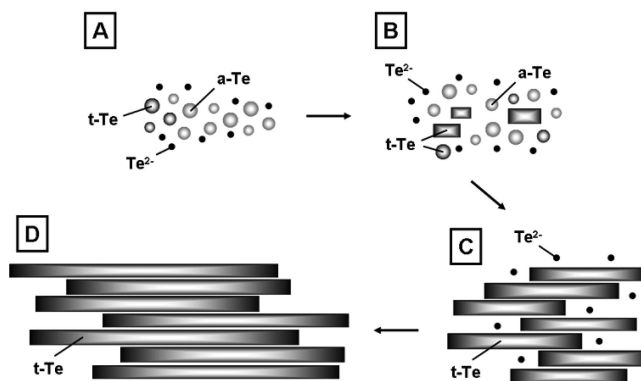
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**ABSTRACT:** We have demonstrated a simple approach to the synthesis of fluorescent trigonal tellurium (t-Te) nanowires in aqueous solution at room temperature. The t-Te nanowires were prepared from the reduction of tellurium dioxide (TeO<sub>2</sub>) with concentrated hydrazine solution through deposition of Te atoms that were reduced from telluride ions (Te<sup>2-</sup>) and dissolved from amorphous tellurium (a-Te) nanoparticles onto t-Te nanocrystallines. By carefully controlling the growth time from 40 to 120 min, we prepared different sizes of t-Te nanowires; the length changed from 251 to 879 nm, while the diameter only grew from 8 to 19 nm. The absorption wavelength against the diameter of t-Te nanowires displays the diameter dependence of band I (<300 nm). On the other hand, the absorption wavelength against the length of t-Te nanowires displays the length dependence of band II (>600 nm). By increasing the size of t-Te nanowires, their absorption is under a red shift. For example, the maximum wavelengths of the absorption bands for the t-Te nanowires with the lengths of 251 nm are 271 and 602 nm, while those for 879 nm t-Te nanowires are at 280 and 687 nm, respectively. Deconvolution of the photoluminescence profile for t-Te nanowires obtained at 120 min yields four Gaussian peaks centered at 334, 397, 460, and 507 nm.

## Introduction

One dimensional (1D) semiconductor nanostructures are interesting and important materials because they are attractive building blocks for assembling active and integrated optoelectronics and transistors in nanoscales.<sup>1–4</sup> Te is a p-type semiconductor having a band gap energy of 0.35 eV and thus it is interesting material for fabricating nanodevices. A layer-by-layer assembly technique was applied to fabricate photoactive Te nanowires/polyelectrolyte thin films.<sup>5</sup> The Te films are activated from off states under light illumination as a result of increases in conductivity.

Because of its unique helical-chain conformation in its crystal structure, Te has a highly anisotropic growth tendency. It has been recognized that Te atoms are bound together through van der Waals interactions in a hexagonal lattice to form 1D structures. Physical deposition has been used to prepare trigonal tellurium (t-Te) nanotubes<sup>6,7</sup> and nanobelts<sup>8</sup> recently, but preparations are usually conducted at high temperatures (>350 °C). Alternatively, different routes have been developed for preparation of t-Te nanostructures at temperatures <200 °C.<sup>9–20</sup> A self-seeding approach was developed for the large-scale synthesis of 1D t-Te nanostructures with diameters ranging from 50 to hundreds of nanometers and lengths up to tens of micrometers in solutions.<sup>9,10</sup> The t-Te nanotubes were obtained through the reduction of orthotelluric acid by ethylene glycol (EG) at a refluxing temperature of 197 °C. By decreasing the concentration of EG, t-Te nanowires were prepared. A hydrothermal method was also demonstrated to synthesize single-crystal t-Te nanobelts (average thickness of 8 nm, width of 30–500 nm, and length of several hundred micrometers) and nanotubes (outer diameter of 150–400 nm, wall thickness of 5–15 nm, and length of 5–10 μm) at 180 °C.<sup>11</sup> A surfactant-assisted growth process was developed for preparation of t-Te

Scheme 1. Illustration of a Plausible Mechanism for the Formation of t-Te Nanowires<sup>a</sup>

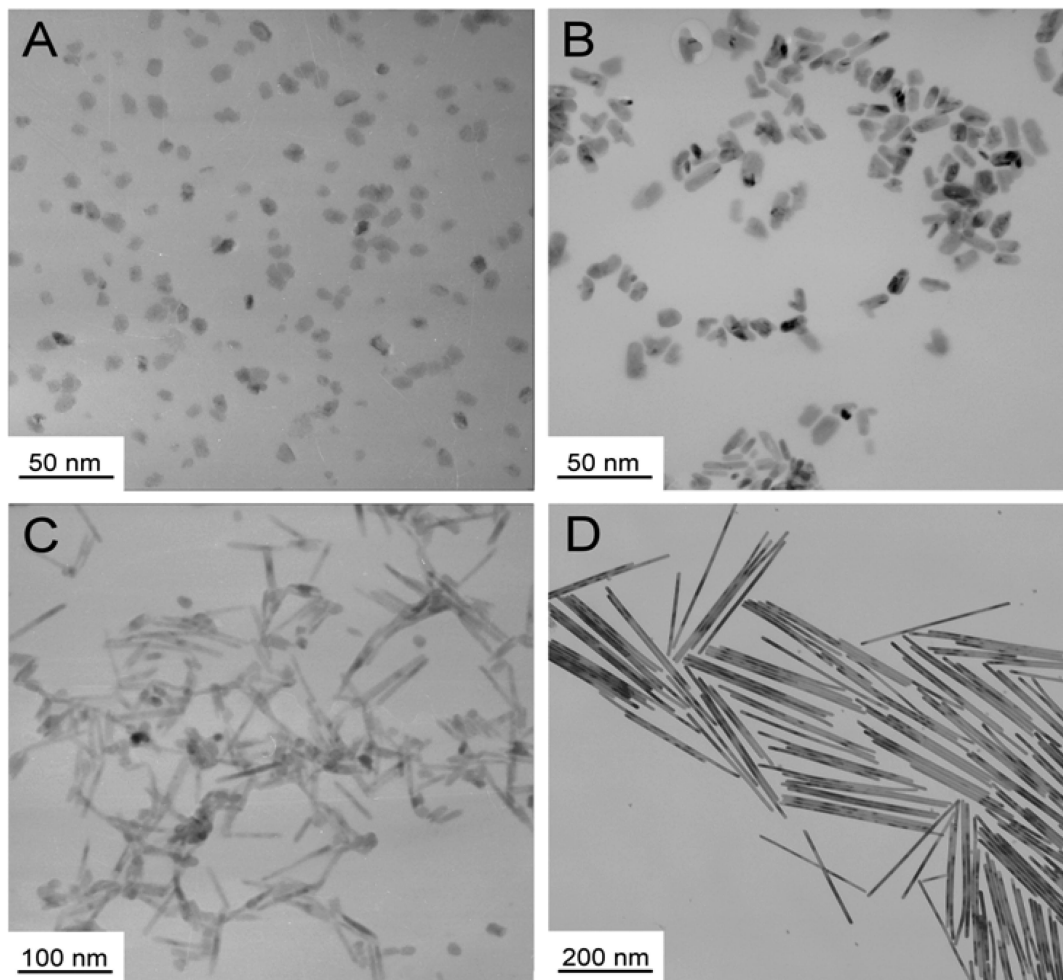
<sup>a</sup> (A) Reduction of TeO<sub>3</sub><sup>2-</sup> with concentrated N<sub>2</sub>H<sub>4</sub> solution at room temperature in an aqueous medium produce Te<sup>2-</sup> and spherical colloids of a-Te and t-Te. (B) t-Te nanostructures were formed from a-Te colloids through SSS transformation. (C) Most a-Te colloids disappeared, and the nanostructures were t-Te nanowires in the solution. (D) t-Te nanowires still grew to extend their length through the deposition of Te atoms that were produced from the oxidation of Te<sup>2-</sup>.

nanorods at 80 °C.<sup>12,13</sup> Both the diameters and lengths of t-Te nanorods decreased with increasing the alkyl length and the polarity of surfactants. Biomolecules (such as alginic acid and amino acid) assisted approaches were used for the synthesis of t-Te nanowires and shuttle-like scrolled Te nanotubes with sharp tips at the temperature range of 150–160 °C.<sup>14–16</sup> A microwave-assisted approach was demonstrated for the synthesis of 20–100 nm of t-Te nanowires in ionic liquid at 180 °C.<sup>17</sup> t-Te nanowires with lengths up to 10 μm were synthesized in starch, a green chemical compound, at 160 °C.<sup>18</sup> In addition, poly(vinylpyrrolidone) was used as a reductant and template for the preparation of Te nanorods, nanowires, and nanotubes over a temperature range of 180–220 °C.<sup>19</sup> Although 1D t-Te nanostructures have been prepared, from a standpoint of green chemistry (energy saving), the development of low-temperature approaches seems to remain a great challenge.

\* To whom correspondence should be addressed. Address: Department of Chemistry, National Taiwan University, 1, Section 4, Roosevelt Road, Taipei 106, Taiwan. Tel./fax: 011-886-2-33661171. E-mail: changht@ntu.edu.tw.

<sup>†</sup> National Taiwan University.

<sup>‡</sup> National Taitung University.



**Figure 1.** TEM images of an aqueous solution containing 10 mM  $\text{TeO}_2$  and 80%  $\text{N}_2\text{H}_4$  after the reaction at room temperature for (A) 10 min, (B) 20 min, (C) 30 min, and (D) 40 min.

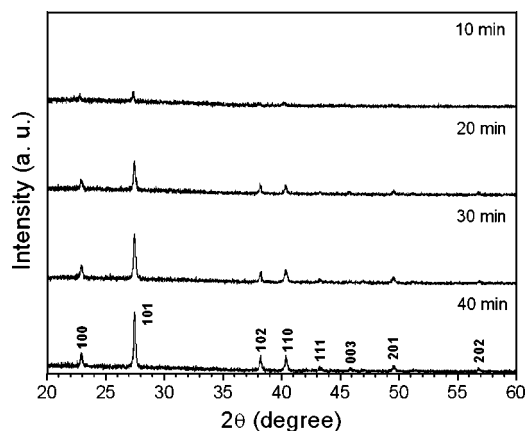
In this paper, we demonstrate a simple route for the synthesis of t-Te nanowires from the reduction of  $\text{TeO}_3^{2-}$  by  $\text{N}_2\text{H}_4$  in aqueous solution at room temperature. The as-prepared blue t-Te nanowires have diameters less than 20 nm and lengths up to 879 nm. By controlling the reaction time between 40 and 120 min, t-Te nanowires with different lengths were prepared, which allowed us to carefully investigate the size-dependent optical properties.

### Experimental Section

**Chemicals.** Sodium dodecyl sulfate (SDS,  $\text{C}_{12}\text{H}_{25}\text{O}_4\text{SNa}$ , 99%) was obtained from Acros. Tellurium dioxide powder (size is unavailable; 99.9%) and hydrazine monohydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , 80%) were purchased from SHOWA (Tokyo, Japan). Deionized water from a Milli-Q ultrapure (18.2 M $\Omega$ -cm) system was used in this study.

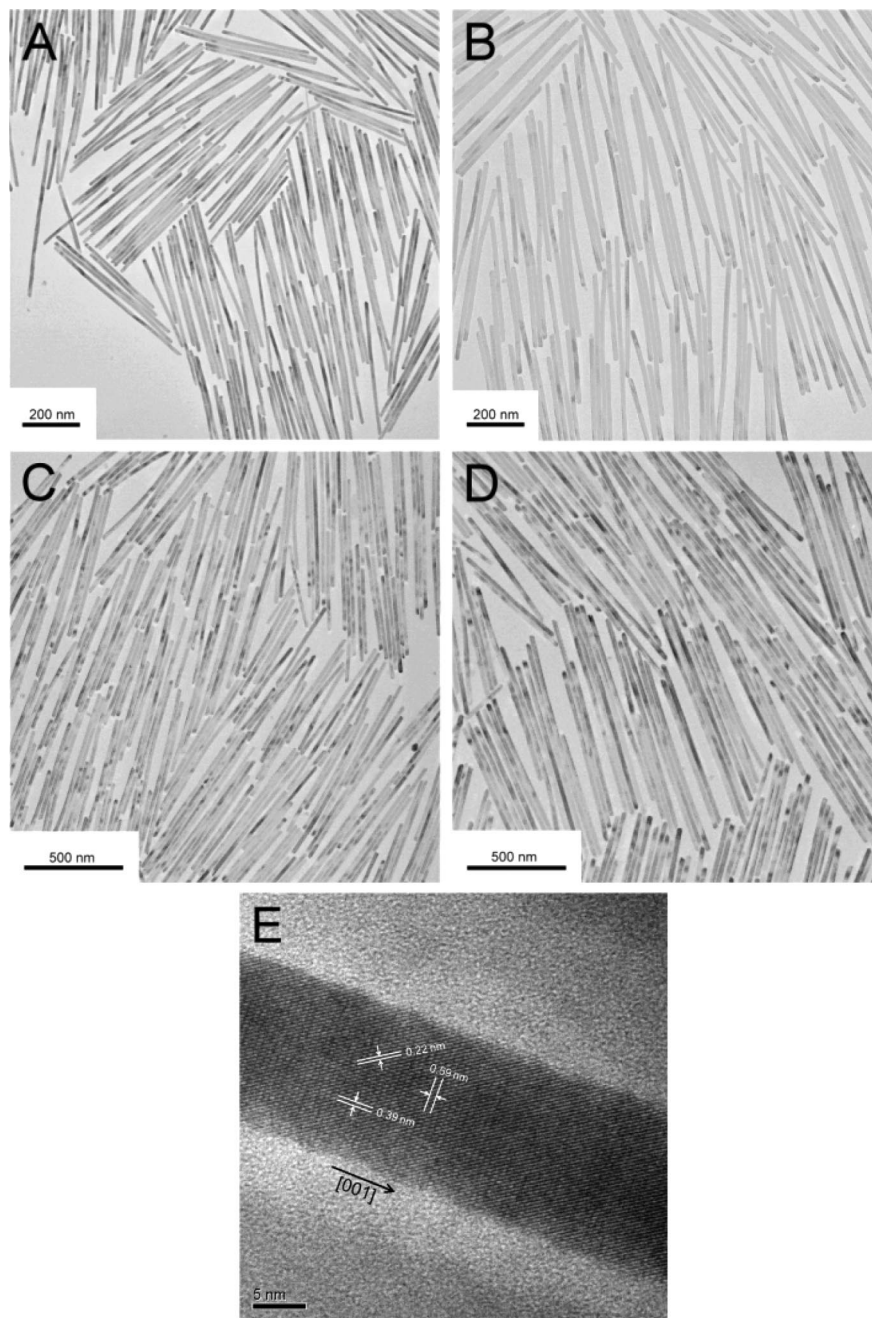
**Synthesis of t-Te Colloids and Nanowires.**  $\text{TeO}_2$  powder (16 mg) was slowly added to 10 mL  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  in a beaker at room temperature under constant magnetic stirring. The powder was completely dissolved within 10 min. The solution sequentially changed colors from colorless, to amber, to purple, and eventually to blue. The blue color indicates the formation of t-Te nanowires. For terminating the reactions, the reaction solutions were diluted 10 times with SDS solutions (10 mM). SDS was added to stabilize the as-prepared t-Te nanowires.

**Characterization of t-Te Nanowires.** JEOL-1200EX II and FEI Tecnai-G2-F20 transmission electron microscopes (TEM) were used to measure the sizes and shapes of the t-Te colloids and nanowires. Prior to TEM measurements, the t-Te colloids and nanowires were subjected to two centrifuge/wash cycles to remove most of the matrices



**Figure 2.** XRD spectra of the reaction mixture of  $\text{TeO}_2$  and  $\text{N}_2\text{H}_4$  following the reaction at room temperature for 10, 20, 30, and 40 min. Other conditions are the same as those described in Figure 1.

such as SDS and hydrazine. The redispersed t-Te colloids and nanowires were then placed on Formvar/carbon film Cu grids (200 meshes) from Agar Scientific Ltd. (Stansted, England) and dried at room temperature. For X-ray diffraction (XRD) measurements using a PANalytical X'Pert PRO diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 0.15418$  nm), the samples were prepared on glass substrates. The UV-vis absorption spectra of the as-prepared t-Te colloids and nanowires were recorded using a double-beam UV-vis spectrophotometer (Cintra 10e, GBC).

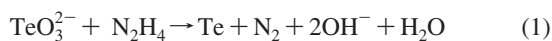


**Figure 3.** TEM images of t-Te nanowires were taken after reactions for different times. (A) 60 min, (B) 80 min, (C) 100 min, and (D) 120 min. Other conditions are the same as those described in Figure 1. (E) HRTEM image of a t-Te nanowire obtained from (D). The interplanar spacings of 0.59, 0.39, and 0.22 nm correspond to the (001), (010), and (110) lattice planes of t-tellurium.

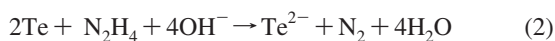
A Hitachi F-4500 spectrophotometer was used for the photoluminescence measurements of t-Te colloids and nanowires.

## Results and Discussion

**Synthesis of Te Nanowires.** When adding  $\text{TeO}_2$  to  $\text{N}_2\text{H}_4$  in aqueous solution under alkaline conditions, metalloid oxyanion tellurite ( $\text{TeO}_3^{2-}$ ) was formed, and it then was reduced by  $\text{N}_2\text{H}_4$  to form Te colloids:

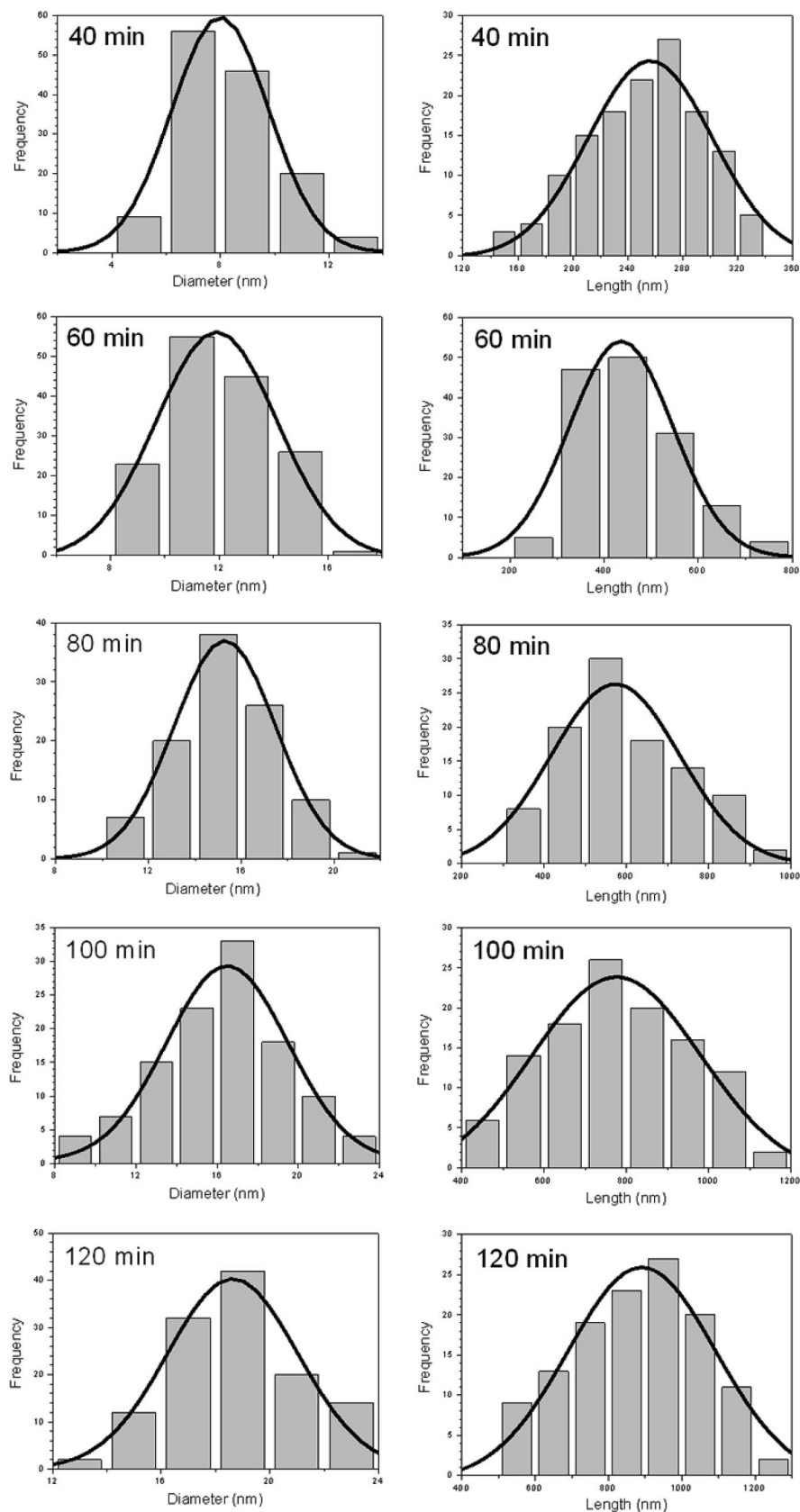


In addition,  $\text{N}_2\text{H}_4$  also reduced Te colloid to  $\text{Te}^{2-}$  under alkaline conditions:



Initially, two types of Te colloids were formed: amorphous Te (a-Te) and t-Te as depicted in Scheme 1. Because a-Te colloids has a higher free energy relative to t-Te colloids, they were dissolved and deposited on t-Te nanocrystallines (served as seeds) for the growth of t-Te nanostructures through a solid-solution-solid (SSS) transformation mechanism.<sup>9,20,21</sup> Once the a-Te colloids were reacted completely,  $\text{Te}^{2-}$  were oxidized by  $\text{O}_2$  to form Te atoms that were then deposited onto the t-Te nanowires. Because t-tellurium has a highly anisotropic structure, the growth direction would be favorably confined to the  $\langle 001 \rangle$  direction, and thus the single crystalline seeds tend to grow into the cylindrical shape. As a result, the length of the t-Te nanowires increased. We point out that the length of t-Te nanowires can be controlled by changing the molar ratio of

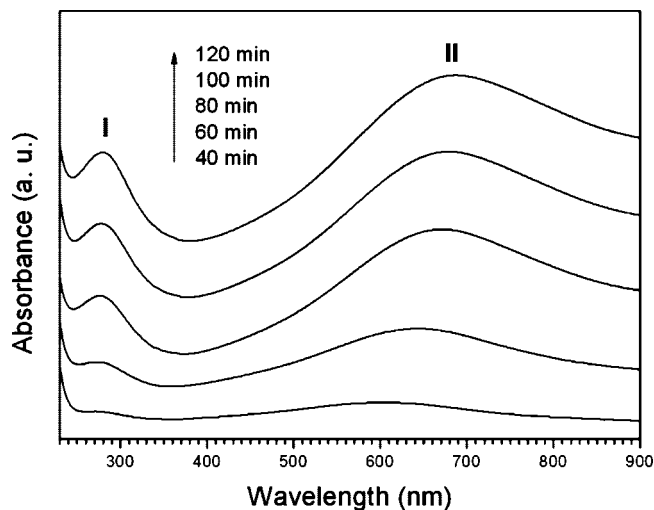




**Figure 4.** Histograms representing the size distribution of the t-Te nanowires.

$\text{TeO}_2/\text{N}_2\text{H}_4$ ; shorter and thicker t-Te nanowires were formed with high molar ratios of  $\text{TeO}_2/\text{N}_2\text{H}_4$ , simply because more amorphous Te (a-Te) and t-Te colloids were formed initially.

The growth mechanism depicted in Scheme 1 is supported by the time-evolution TEM images of Te nanostructures displayed in Figure 1. The growth was stopped by diluting the



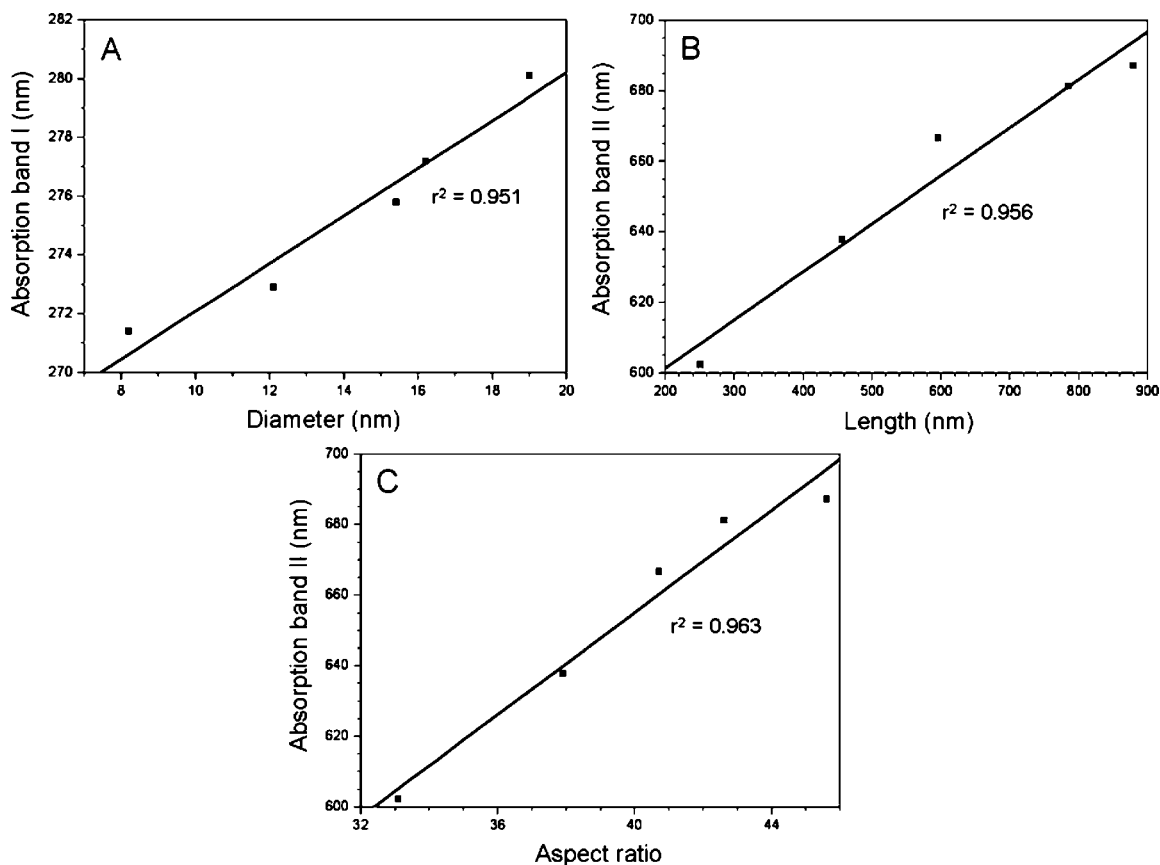
**Figure 5.** UV-vis absorption spectra of t-Te nanowires that were prepared for different reaction times (40–120 min). Peak I represents the transition from VB2 to CB1, and peak II represents the transition from VB3 to CB1. Other conditions are the same as those described in Figure 1.

solutions 10 times with 10 mM SDS solution in which the redox reaction speed was fairly slow. Over the time course of 0–10 min, a-Te and t-Te colloids with diameters less than 7 nm were formed. Over the reaction period of 10–30 min, a-Te colloids were dissolved, and the Te atoms were deposited onto t-Te colloids. The t-Te nanorods (reaction time 30 min) have an

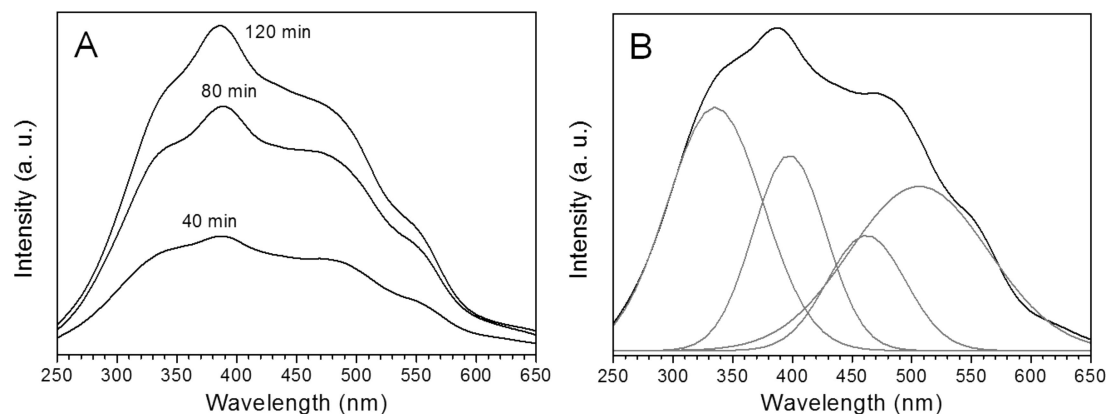
average diameter of 6.9 ( $\pm 2.3$ ) nm and an average length 51.3 ( $\pm 15.4$ ) nm. Since there were few t-Te nanorods in existence after reaction for 40 min, we suggest that the growth of t-Te nanowires having an average diameter of 8.2 ( $\pm 1.7$ ) nm and an average length of 251 ( $\pm 42$ ) nm from t-Te nanorods occurs through deposition of Te atoms from  $\text{Te}^{2-}$ .

We determined the concentration of Te ions in the supernatant to be  $1.01 \times 10^3$  ppm after the solution was subjected to centrifugation at 15 000 rpm for 10 min. The yield for the preparation of t-Te nanowires is quite high (close to 100%). The powder-XRD spectra for the corresponding Te colloids (reaction times 10–40 min) depicted in Figure 2 further support our proposed mechanism. The (101) peak is assigned to be for t-Te nanorods. With increasing reaction time, the intensities for (100), (102), (110), (201) peaks increased, showing an increased proportion of t-Te nanorods and nanowires. The peaks (111), (003), (202) are characteristic of a trigonal phase of t-Te nanowires.

**Length Control of t-Te Nanowires.** The time-evolution TEM images shown in Figure 1 suggest that the length of t-Te nanowires can be tuned by carefully controlling the reaction time. It is noted that the growth of t-Te nanowires is much slower and the size distribution becomes broader after reaction times longer than 120 min. We conducted reactions under the same conditions for different times (60, 80, 100, and 120 min). As expected, the lengths of 1D t-Te nanowires increased with increasing reaction time (Figure 3). The lengths for t-Te nanowires obtained at the reaction times 60, 80, 100, and 120 min are 456 ( $\pm 110$ ), 595 ( $\pm 150$ ), 785 ( $\pm 170$ ), and 879 ( $\pm 170$ ) nm, respectively. Unlike the change in the length, their diameters



**Figure 6.** (A) Plot of the wavelength of peak I versus the average diameter of the t-Te nanowires. (B) Plot of the wavelength of peak II versus the average length of the t-Te nanowires. (C) Plot of the wavelength of peak II versus the average aspect ratio of the corresponding t-Te nanowires.



**Figure 7.** (A) Photoluminescence spectra of t-Te nanowires that were prepared for different reaction times. Excitation wavelength was set at 210 nm. (B) Deconvolution of the band gives four Gaussian bands centering at 334, 397, 460, and 507 nm, respectively. Other conditions are the same as those described in Figure 1.

did not change significantly: 12.1 ( $\pm 1.9$ ) nm (60 min), 15.4 ( $\pm 2.2$ ) nm (80 min), 16.2 ( $\pm 3.1$ ) nm (100 min), and 19.0 ( $\pm 2.6$ ) nm (120 min). Histograms representing the size distribution of the as-prepared t-Te nanowires were shown in Figure 4, showing that the size distributions of the as-prepared t-Te nanowires are not small. However, when compared to the reported methods,<sup>13,16</sup> the present method provides a more precise size-controlled result. The high resolution transmission electron microscopy (HRTEM) image in Figure 3E shows interplanar spacings of 0.59, 0.39, and 0.22 nm, which correspond to the (001), (010), and (110) lattice planes of t-Te nanowires obtained at the reaction time of 120 min. The crystals are structurally uniform, and there is no dislocation or other planar defects. All these data indicate that t-Te nanowires are single crystallines.

**Optical Properties of t-Te Nanowires.** Te is a p-type semiconductor (bulk Te has a broad absorption band around 300 nm), thus it is interesting to investigate the optical properties of t-Te nanowires. An absorption band over the range of 250–350 nm and photoluminescence with the emission wavelength centered at 700 nm for t-Te nanorods have been reported.<sup>22</sup> Ultrathin t-Te nanowires (diameter 4–9 nm) possess two broad absorption bands centered at 278 and 586 nm, and two strong emission bands over the range of 390–550 nm have been separately demonstrated.<sup>23</sup> However, the size dependence of the optical properties for t-Te nanowires have not been under careful investigation, mainly because monodispersed t-Te nanostructures having different sizes over a wide range are not available. Figure 5 shows the absorption spectra of t-Te nanowires of different sizes. According to the Hartree–Fock–Slater study,<sup>24</sup> peak I (in the range of 3–6 eV) is due to the transition from the valence band (p-bonding VB2) to the conduction band (p-antibonding CB1), and peak II (in the range of 0–3 eV) is assigned to be the transition from the valence band (p-lone-pair VB3) to the conduction band (p-antibonding CB1). The linear plot ( $R^2 = 0.951$ ) of the absorption wavelength against the diameter of t-Te nanowires displays the diameter dependence of peak I (Figure 6A). On the other hand, the linear plot ( $R^2 = 0.956$ ) of the absorption wavelength against the length of t-Te nanowires displays the length dependence of peak II (Figure 6B). To the best of our knowledge, this is the first example experimentally showing the impacts that the diameter and length of t-Te nanowires have on absorption. A previous report only showed the correlation between the diameter and peak I.<sup>22</sup> Indeed, peak II undergoes red shifts by increasing their aspect ratios (Figure 6C). Figure 7 exhibits the photoluminescence of different sizes of t-Te nanowires when they were excited at 210 nm. With increasing reaction time, the photolu-

minescence profiles for t-Te nanowires are similar, but the intensity increases. We point out that the size of t-Te nanowires increases with increasing reaction time. Deconvolution of the photoluminescence band for 1D t-Te nanowires obtained at 120 min yields four Gaussian peaks centered at 334, 397, 460, and 507 nm (Figure 7B). Three of these photoluminescence peaks can be attributed to imperfections associated with semiconductor nanorods.<sup>25</sup> The 334 nm peak is close to the absorption peak I and thus can be assigned to an excitonic transition. The peak is notably higher than the free excitonic transition in bulk Te at room temperature.

## Conclusion

We report a simple approach to the synthesis of fluorescent t-Te nanowires at room temperature. By using concentrated  $N_2H_4$  solution as the reducing agent, preparation of t-Te nanowires from  $TeO_2$  powder was completed within 2 h. From the standpoint of green chemistry, this simple approach is advantageous over standard methods in terms of energy saving. By controlling the reaction time, different lengths of t-Te nanowires were prepared. Our results clearly demonstrated the size dependence of absorption properties of t-Te nanowires for the first time. Having unique fluorescence properties, the as-prepared t-Te nanowires hold great potential for fabrication of nanodevices.

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