

Preparation by Hydrothermal Techniques in a Tungstosilicate Acid Solution System and Optical Properties of Tellurium Nanotubes

Li Zhang,^{*,[a]} Cong Wang,^[a] and Deyun Wen^[a]

Keywords: Nanotubes / Tellurium / Polyoxometalates

Single-crystalline tellurium nanotubes can be easily synthesised by a simple hydrothermal, economical and green chemical route. The tungstosilicate acid (TSA) serves as not only an effective reducing agent but also a new morphology-directing agent for tellurium nanotubes from sodium tellurate (Na_2TeO_3) precursor powders. Scanning electron microscopy images show that most of the tellurium nanotubes have sloping cross-sections and open ends with outer diameters of 100–500 nm, wall thicknesses of 30–100 nm and lengths of 30–50 μm . A few Te nanotubes have hexagonal cross-

sections. Te nanotubes grow along the [001] direction and have excellent crystallinity. The synthetic conditions also investigated for the tellurium nanotubes were molar ratio of sodium tellurate to TSA, pH of reaction solution and reaction temperature. The optical properties of the *t*-Te nanotubes have been investigated. A possible mechanism for the growth of tellurium nanotubes has been discussed.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2009)

Introduction

In recent years nanomaterials, especially 1D nanostructures such as nanowires, nanorods, nanobelts and nanotubes have attracted much interest due to their distinct physical and chemical properties and potential applications in nanoscale devices.^[1,2] Elemental tellurium is a narrow bandgap semiconductor with a direct bandgap energy of 0.35 eV. Trigonal tellurium has a highly anisotropic crystal structure consisting of helical chains of covalently bound atoms which are in turn bound together through van der Waals interactions into a hexagonal lattice.^[3] This inherent anisotropy makes these materials ideal candidates for generating a 1D nanostructure.^[4] Trigonal tellurium exhibits many useful and interesting properties for example, photoconductivity and catalytic activity toward some reactions, thermoelectricity, high piezoelectricity and nonlinear optical responses.^[5] In the past decade, 1D tellurium nanocrystals have been synthesised by different routes such as solvothermal or hydrothermal methods,^[6] microwave-assisted methods,^[7] chemical (physical) vapour deposition^[8] etc. Xia and coworkers first reported that Te nanotubes with blocking seeds (Te atom clusters) within could be obtained by adding orthotelluric acid to pure ethylene glycol heated to reflux at 197 °C.^[9] Mo and coworkers synthesised

Te nanotubes by in situ disproportionation of sodium tellurite (Na_2TeO_3) in an aqueous ammonia system at 180 °C.^[6] Yu and coworkers have synthesised the single-crystalline trigonal tellurium (*t*-Te) nanotubes by reducing TeO_2 using ethylene glycol (EG) as a reducing agent. The Te nanotubes obtained in this approach display strong luminescent emission in the blue-violet region and strong corrosion resistance in ethanol.^[10] Recently, it has been shown that the Te nanotubes synthesised by chemical methods could contain tiny amounts of impurities which could result in dramatic changes in the conducting properties.^[10c] Komarneni and coworkers reported a green chemical approach to the synthesis of tellurium nanowires by using starch as a reducing agent^[11] whereas Wang and coworkers reported the PEG-mediated hydrothermal growth of single-crystal tellurium nanotubes.^[12] All these studies indicated that the growth processes of tellurium nanotubes were still diverse under different synthetic conditions. At present developing novel, simple and convenient methods for synthesising nanomaterials, especially 1D nanostructures, is still a challenge for chemists and materials scientists.

Polyoxometalates of the Keggin structure have the general formula $(\text{XM}_{12}\text{O}_{40})^{(8-n)-}$ where ‘M’ stands for W or Mo and ‘X’ stands for heteroatoms such as P, Si, Ge with ‘*n*’ being the valency of X.^[13,14] It is well known that Keggin ions undergo stepwise multielectron redox processes without a structural change.^[15,16] They may be reduced electrolytically, photochemically and chemically (with suitable reducing agents). These metal oxygen cluster anions with well defined structures and properties represent a large category and they have extensive applications in the fields of analytical chemistry, biochemistry and solid state devices, and have

[a] Anhui Key Laboratory of Spin Electron and Nanomaterials (Cultivating Base), Department of Chemistry & Biology, Suzhou University, Suzhou 234000, P. R. China
Fax: +86-557-2871003
E-mail: zhhsuzh@163.com

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejic.200900143>.

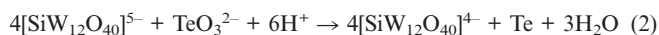
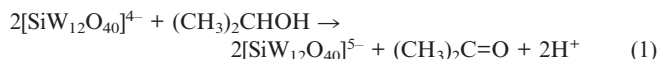
been used as antiviral and antitumor reagents. Their redox chemistry is characterised by their ability to accept and release a certain number of electrons, in distinct steps, without decomposition.^[16] Tungstosilicate acid (TSA) is one of the simplest polyoxometalates with the Keggin structure.

Recently, Papaconstantinou and coworkers discovered that photochemically reduced polyoxometalates with the Keggin structure of phosphotungstic acid $[(PW_{12}O_{40})^{3-}]$ lead to the formation of the corresponding metal nanoparticles.^[17] Sastry and coworkers used $PW_{12}O_{40}^{3-}$ ions to make phase-pure core-shell nanoparticles^[18,19] and they also used $PW_{12}O_{40}^{3-}$ as a template for the in situ growth of metal nanoparticles,^[20,21] star-shaped calcium carbonate crystals^[22] and CdS nanoparticles.^[23] Yang and coworkers prepared the 3D packed trigonal selenium microspheres by a hydrothermal process^[24] and, recently, we have synthesised a tungstosilicate acid (TSA)-Ag nanocomplex based on the reduction of silver nitrate by a UV-irradiated tungstosilicate acid solution.^[25] The size of the nanocomplex was in the range of 20–60 nm, with a mean diameter of 45 nm. Multi-charged TSA-Ag composite nanoparticles were alternately deposited with oppositely charged chitosan in a layer-by-layer assembly.

Herein we report a facile, economical and green chemical route for the synthesis of tellurium nanotubes. Single-crystalline tellurium (*t*-Te) nanotubes with a sloping cross-section or a hexagonal cross-section can be synthesised on a large scale by the reaction of tungstosilicate acid and sodium tellurate solutions under hydrothermal conditions wherein the TSA plays the role of a reducing agent, a soft template and a solvent. To the best of our knowledge, this is the first study of the synthesis of single-crystalline Te nanotubes by using templates of Keggin ion colloidal particles. The optical properties of *t*-Te nanotubes have also been investigated.

Results and Discussion

A representative Keggin structure $(SiW_{12}O_{40})^{4-}$ ion was used to study the reaction between $(SiW_{12}O_{40})^{5-}$ ions and TeO_3^{2-} ions. The $(SiW_{12}O_{40})^{5-}$ ion was obtained by hydrothermal treatment of a deaerated 2-propanol/ $(SiW_{12}O_{40})^{4-}$ / TeO_3^{2-} aqueous solution, in the presence of, for instance, 2-propanol as a sacrificial reagent [Equation (1)].^[17,26] With hydrothermal treatment, the above-described solution gradually turned from colourless to silver-gray as TeO_3^{2-} ions were reduced to Te metal [Equation (2)].



There are two reasons for the result: one is the ability of the $(SiW_{12}O_{40})^{5-}$ to transfer electrons efficiently to TeO_3^{2-} ions. The other is the lower potential of the one-equivalent-reduced tungstate couple $(SiW_{12}O_{40})^{4-}/(SiW_{12}O_{40})^{5-}$ (0.057 V vs. NHE) relative to TeO_3^{2-}/Te (0.827 V vs.

NHE).^[27] Furthermore, TSA ions can be utilised cyclically as oxidising or reducing agents according to equations 1 and 2 whilst the structure of $(SiW_{12}O_{40})^{4-}$ remains unchanged.

The influence of the reaction temperature on the formation of tellurium nanotubes was examined. The reaction cannot take place when the temperature is below 180 °C. In the XRD pattern, the characteristic Te diffraction peaks cannot be observed (see XRD pattern in Figure S1 in the Supporting Information). If the temperature is up to 200 °C, the *t*-Te tubes can be obtained (as shown in Figure 1).

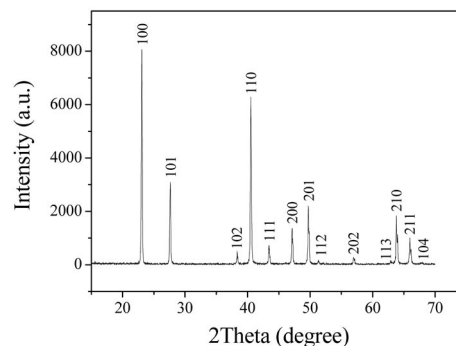


Figure 1. XRD pattern of the prepared tellurium nanotubes.

The composition and phase of the resultant samples were examined by XRD. Figure 1 shows the XRD pattern of the resultant sample. All diffraction peaks can be readily indexed as the hexagonal phase of tellurium with lattice constants $a = 0.4459$ nm and $c = 0.5921$ nm which are in agreement with the reported values of $a = 0.4458$ nm and $c = 0.5927$ nm (JCPDS, 36–1452). No other impurity was indicated by the X-ray diffraction pattern. Compared with the standard pattern of hexagonal phase tellurium, unusually strong (*h*00) reflection peaks and weak (*h**k**l*) reflection peaks ($l \neq 0$) were observed in the XRD pattern.

The morphology and dimension of the samples were examined by FESEM. Figure 2 (a) shows that the product obtained is composed of 1D nanomaterials with lengths in the range of 30–50 μm. Parts b, c and d of Figure 2 show the FESEM images with higher magnification indicating that the resultant tellurium sample is mainly composed of irregular hexagonal prism nanotubes with sloping cross sections. Some tellurium nanotubes show hexagonal cross sections (as indicated by arrow 1 in Figure 2, b). Most of the nanotubes have outer diameters in the range of 100–500 nm and wall thicknesses in the range of 30–100 nm. Figure 2 (b) shows that some tiny spherical nanoparticles can be found on the surface of the sample (as indicated by arrow 2). It should be amorphous tellurium dioxide because of the oxidation of Te tubes during the storage period.^[10]

The microstructure and growth direction of the tellurium nanotubes were studied by HRTEM and SAED. Figure 3 shows a typical transmission electron microscope (TEM) image and high-resolution TEM (HRTEM) image of the obtained sample, along with the electron diffraction (SAED) pattern of the selected area. The TEM images in

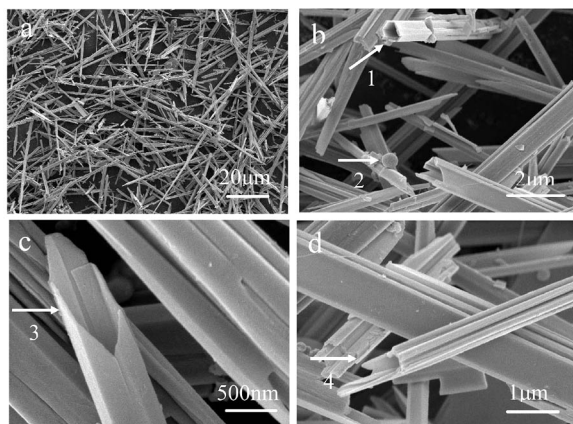


Figure 2. FESEM images with different magnifications of the tellurium nanotubes (a): low-magnification FESEM image of the prepared tellurium nanotubes; (b) (c) (d): FESEM image at high magnification.

Figure 3 (a, b) show that the Te nanostructures are tubelike and the tubes are genuinely hollow and contain no blocking seeds within. Figure 3 (b) shows an individual Te nanotube with a well-defined tubelike morphology and an outer diameter of ca. 300 nm. No obstruction was found within the tube. The SAED pattern in Figure 3 (c) was taken on a typical individual nanotube, showing that the nanotube is single crystalline with growth along the [001] direction. The HRTEM image in image d in Figure 3 show lattice spacings of ca. 2.23 and 5.95 Å corresponding to the lattice spacings of the (110) and (001) planes, respectively, for trigonal tellurium. The combination of the results by HRTEM, XRD and the SAED pattern confirm that the axis of the nanotube is along the [001] direction. This result confirms that single-crystalline tellurium nanotubes with a sloping cross sections can be synthesised on a large scale from a commercial TeO_3^{2-} precursor by using TSA as a reducing agent.

Figure 4 shows the FESEM images of tellurium nanotubes synthesised with different molar ratios of TeO_3^{2-} ions to TSA at 200 °C for 20 h. Parts a–h of Figure 4 show four samples of Te nanotubes corresponding to molar ratios of 1:2, 1:4, 1:10 and 4:1. There are some morphology changes between this samples and the sample of Figure 2. The lengths of these samples are in the range of 3–30 μm. As demonstrated in images a and b, many small nanoparticles have been found on the surfaces of the sample which may be amorphous tellurium dioxide formed during the storage period. When the molar ratio of TeO_3^{2-} ions to TSA is 1:4, the Te nanotubes with a sloping cross-sections were obtained (images c and d in Figure 4). When the molar ratio of TeO_3^{2-} ions to TSA is to 1:10, a remarkable change in morphology occurred. A tri-tipped tubular structure was observed. When the molar ratio of TeO_3^{2-} ions to TSA is 4:1, the Te nanotubes with an irregular cross-sections were obtained. However, the lengths of the tubes is diverse and in a wide range and some flakes are also obtained (images f and h in Figure 4). The above results indicate that the molar ratio of TeO_3^{2-} ions to TSA is influential in the for-

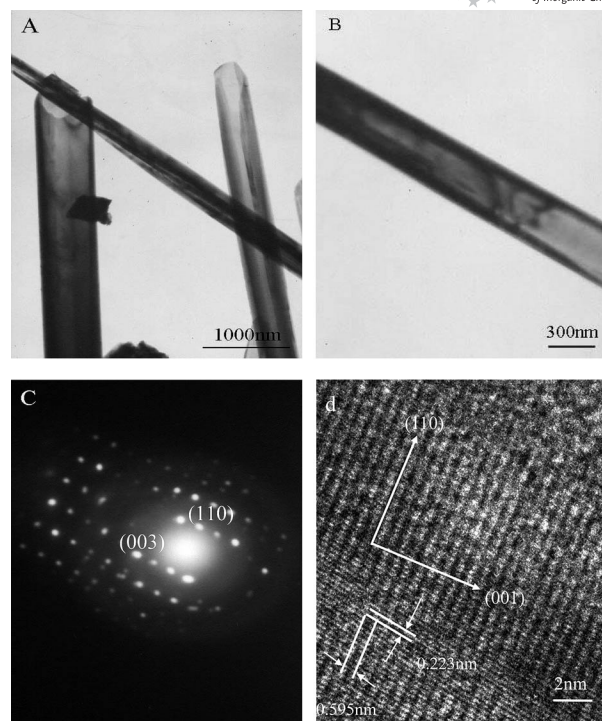


Figure 3. (a) TEM images of the Te nanotubes and (b) an individual Te nanotube; (c) SAED pattern taken on the Te nanotube shown in (b); (d) HRTEM image of the tellurium nanotube.

mation of Te nanotubes. This behaviour is similar to that found in many chemical reduction approaches to nanosystems because the nucleation and growth sequences are affected both by the relative concentrations of the reducing agent and the precursor.^[24]

The dependence of the products on the pH of the solution was also studied. The FESEM images show the prepared white products corresponding to pH values of 3.62 (a) and 4.45 (b) (as shown in Figure S2 in the Supporting Information). The products are composed of irregular and jujube-like particles. In the XRD pattern (see XRD pattern in Figure S3 in the Supporting Information) all peaks can be indexed to the orthorhombic phase of paratellurite (TeO_2) with cell parameters $a = 12.0$ Å, $b = 5.46$ Å and $c = 5.61$ Å which are in good agreement with the standard literature data (JCPDF card number: 74–1131). The enhanced relative intensities of the (h 00) diffraction peaks compared with those for the standard indicated the possible preferential orientation of the crystals. The stability of TSA changes with the pH of the solution – controlling the pH of $(\text{SiW}_{12}\text{O}_{40})^{4-}$ solution is important in the synthesis nanostructure materials. TSA is stable up to a pH of about 5,^[28] the pH values of the 5 mM TSA and 5 mM sodium tellurate solutions were maintained at 1.82 in this experiment. We suppose that TSA decomposed when the pH value of the solution was adjusted to 3.62 or 4.45 using NaOH. An increase in the pH value does alter the redox power of TSA and this leads to the synthesis of TeO_2 not Te.

To obtain further evidence for the purities and compositions of the products, X-ray photoelectron spectra (XPS)

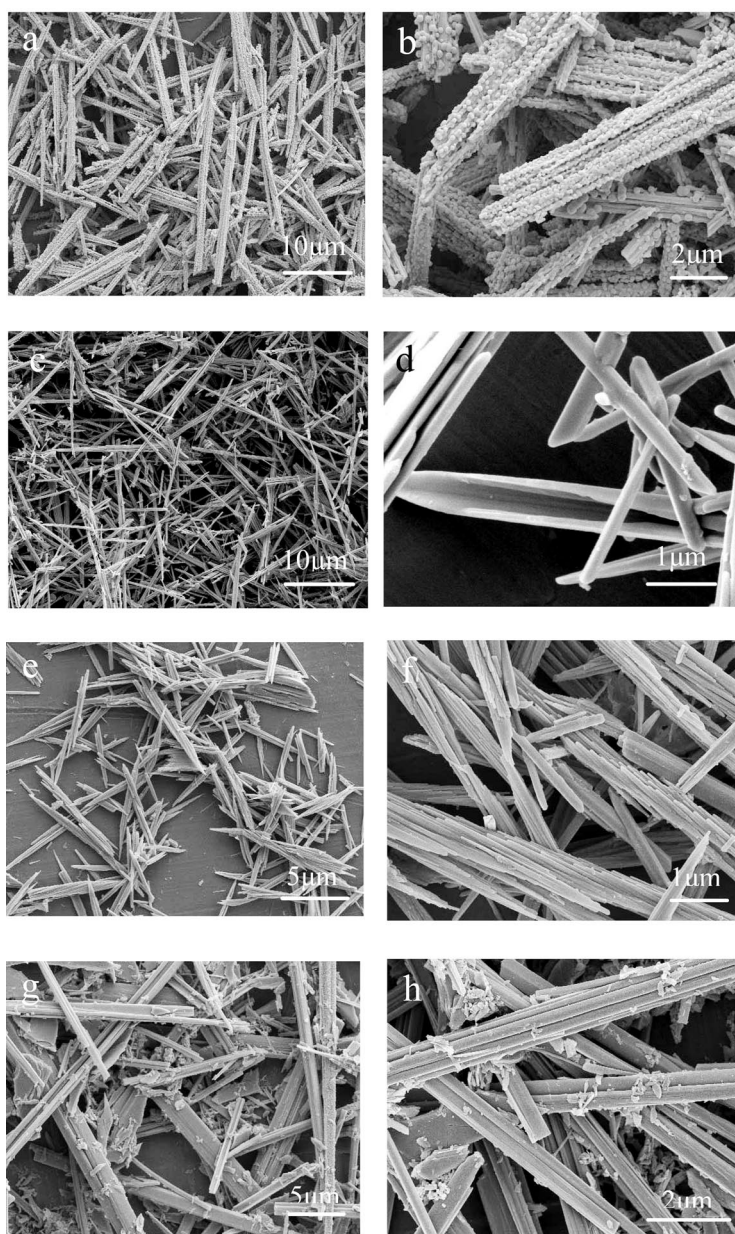


Figure 4. FESEM images of tellurium nanotubes synthesised with different molar ratios of TeO_3^{2-} ions to TSA at 200 °C for 20 h: (a, b) 1:2, (c, d) 1:4, (e, f) 1:10 and (g, h) 4:1. ($[\text{TeO}_3^{2-}] = 5 \text{ mM}$).

were recorded. The spectroscopic survey of the products stored in air for one month showed the presence of C_{1s} (BE = 284.82 eV), Te_{4d} (BE = 41.0 eV), Te_{3d} (BE = 573.19 eV) and O_{1s} (BE = 531.07 eV) core levels with no evidence of impurities (see Figure 5, a). Part b of Figure 5 shows the Te_{3d} core-level spectrum with four peaks centred at binding energies of 573.19, 576.65, 583.6 and 587.15 eV. Two strong peaks at 573.19 and 583.6 eV correspond to the Te^0 3d binding energy, two weak peaks at 576.65 and 587.15 eV can be assigned to the Te^{IV} 3d binding energy. The spectrum in Figure 5 (b) shows the presence of both the elemental tellurium 3d_{5/2} peak (573.19 eV) and a small amount of oxidised tellurium (576.65 eV) which is consistent with that for TeO_2 reported by S. H. Yu and coworkers.^[10]

Room-temperature photoluminescence spectroscopy of the tellurium nanostructures was reported previously.^[6c] The concentration dependence of the photoluminescence spectra of the obtained Te nanotubes is depicted in Figure 6. The photoluminescence intensity increases with the concentration of the obtained Te nanotubes in absolute ethanol solution. The excitation spectrum of the *t*-Te nanotubes show one strong peak and one weak peak at 275 and 301 nm, respectively, at a wavelength of 332 nm (Figure 6, a) which is consistent with that for ultrathin nanowires reported by S. H. Yu and coworkers.^[6c] Two strong photoluminescence emission peaks at 335 and 405 nm with an excitation wavelength of 273 nm were observed for the *t*-Te nanotubes (Figure 6, b). Apparently, different from the re-

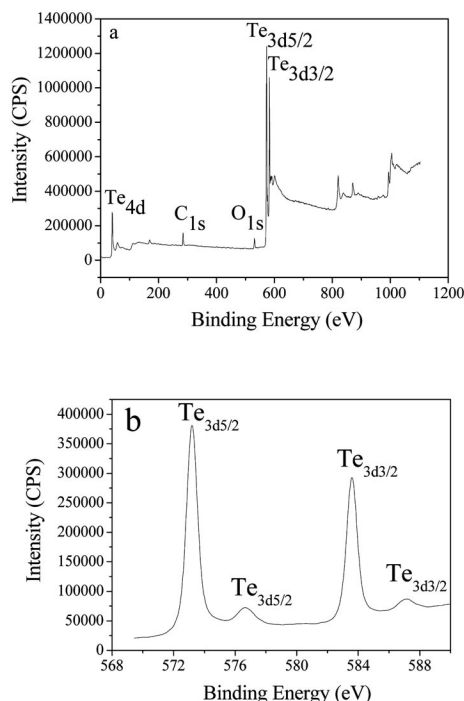


Figure 5. XPS core level spectra recorded from the Tellurium nanotubes after being stored in air for one month. (a) Survey of the sample; (b) survey of the Te_{3d} region.

sults obtained by H. T. Chang and coworkers,^[29] deconvolution of the photoluminescence band for 1D *t*-Te nanowires obtained at 120 min yields four Gaussian peaks centred at 334, 397, 460, and 507 nm.^[29] The differences in the emission peaks might be associated with the thickness of the nanostructures and crystallisation behaviour of 1D nanostructures.

The Raman scattering spectrum taken for the synthesised *t*-Te is depicted in Figure 7. The characteristic vibration peaks at 119.7 and 135.4 cm^{-1} were observed at room temperature. A similar observation was made by S. H. Yu and coworkers who reported peaks at 114.8 and 134.4 cm^{-1} .^[10a] It is reasonable to attribute these bands to A1 bond bending and A1 bond stretching modes or the E mode of the *t*-Te tubes, respectively. The peaks at 260.05 cm^{-1} can be assigned as the second-order spectra of *t*-Te.

Although the exact mechanism of the formation of tellurium nanotubes is difficult to know, we think that the TSA plays an important role in the formation of tellurium nanotubes. A reasonable route is presented. First, TeO_3^{2-} ions are absorbed onto the surfaces of the TSA colloidal particles' templates then converted quickly to Te atoms in a short time under hydrothermal conditions. The tellurium atoms then recrystallise into spherical seeds. It is known that tellurium has infinite helical chain conformation in its crystal structure. Hence it has a strong tendency to grow along the *c* axis direction into a 1D structure. Under hydrothermal conditions, the spherical tellurium seeds will keep on growing with continuous feeding of tellurium atoms and finally grow into tellurium nanotubes.

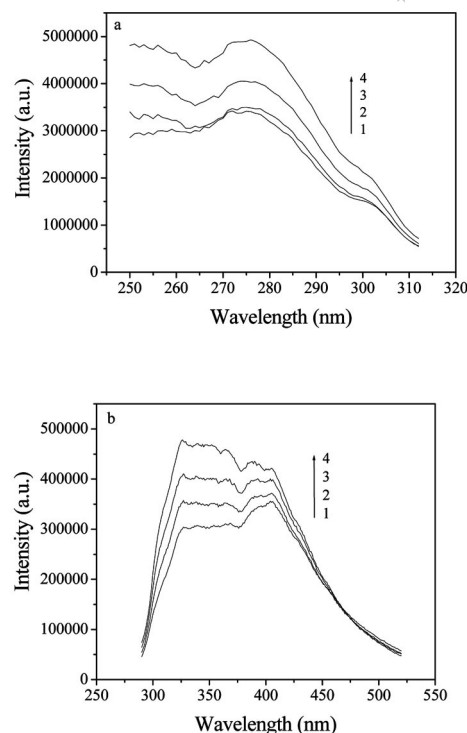


Figure 6. (a) Concentration dependence of photoluminescence excitation spectrum of the obtained Te nanotubes with emission at 332 nm. (b) Concentration dependence of the photoluminescence emission spectrum of Te nanotubes with an excitation wavelength of 273 nm. The curves from bottom to top correspond different concentration of Te nanotubes in absolute ethanol solution (1, $6.5308 \times 10^{-5} \text{ mol L}^{-1}$; 2, $1.3062 \times 10^{-4} \text{ mol L}^{-1}$; 3, $1.9592 \times 10^{-4} \text{ mol L}^{-1}$; 4, $2.6123 \times 10^{-4} \text{ mol L}^{-1}$).

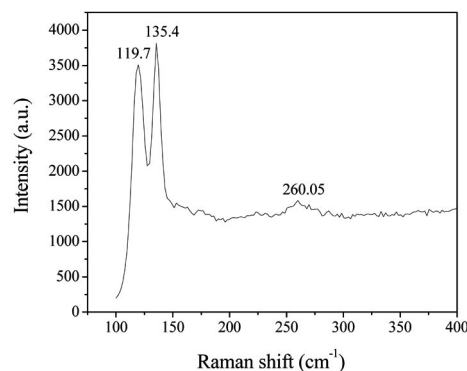


Figure 7. Raman scattering spectrum of tellurium nanotubes.

Conclusions

In summary, single-crystalline trigonal tellurium (*t*-Te) nanotubes with a sloping cross-section or a hexagonal cross-section can be synthesised on a large scale by reaction of a mixture of tungstosilicate acid and Na_2TeO_3 solutions under hydrothermal conditions, wherein the TSA plays the role of a reducing agent and a soft template. Different morphologies of the single-crystalline tellurium can be successfully synthesised by varying the reaction conditions. With unique fluorescence properties, the resultant *t*-Te nanowires

hold great potential for fabrication of nanodevices. This method enlarges the application of polyoxometalates to the green synthesis of nanostructures with low dimensionality and by using the above method, other nanomaterials could be possibly synthesised under very mild and economical conditions.

Experimental Section

Materials: Tungstosilicate acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, TSA), sodium tellurate (Na_2TeO_3), and 2-propanol [$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$] were all A.R. grade and obtained from Shanghai Reagent Co. All the reagents were used without further purification.

Synthesis of *t*-Te Nanotubes: In a typical experiment, aqueous de-aerated solutions of TSA (50 mL, 5 mM) and aqueous Na_2TeO_3 (50 mL, 5 mM) were taken in a test beaker. An aliquot of 2-propanol (5 mL) was added to the 100 mL mixed aqueous de-aerated solution of Na_2TeO_3 and TSA under continuous stirring for 10 min and the solution was then allowed to age for 30 min. The mixed solutions (20 mL) were added into a 25 mL Teflon[®]-lined stainless-steel autoclave and the reaction mixture formed a homogeneous white suspension under vigorous stirring. The autoclave was sealed and maintained in an oven at 200 °C for 20 h and then naturally cooled to room temperature. Silver-gray solids were obtained and collected by centrifugating the reaction mixture. The particles were then washed with distilled water and absolute ethanol several times and dried in a vacuum at 60 °C for 6 h before further characterisation.

The processes for the corresponding control experiments under different reaction conditions, such as molar ratio of sodium tellurate to TSA, pH of reaction solution and reaction temperature were similar to the experiments described above. The mixed solutions had the pH adjusted after 10 min of stirring and 30 min of aging.

To discount the possibility of hydrothermal 2-propanol being the reducing agent for TeO_3^{2-} ions and thus for tellurium nanotubes formation, a control experiment was performed in which 2-propanol (2 mL) was added to an aqueous, de-aerated solution of sodium tellurate (20 mL, 1 mM) which was then hydrothermally treated for 20 h. There was no change in colour of the TeO_3^{2-} solution and no silver-gray solids obtained after hydrothermal treatment indicating that the product of hydrothermally treated 2-propanol is not responsible for the reduction of TeO_3^{2-} .

Transmission Electron Microscopy (TEM) Measurements: Transmission electron microscope (TEM) images were taken with a Hitachi H-800 transmission electron microscope at an acceleration voltage of 200 kV. High resolution transmission electron microscope (HRTEM) analysis and selected area electron diffraction (SAED) patterns were performed on a JEOL-2010 transmission electron microscope.

Field Emission Scanning Electron Microscopic (FESEM) Measurements: The size and morphology were analysed by using a Sirion 200 (FEI Co., Ltd.) field emission scanning electron microscope at an accelerating voltage of 5.0 kV.

X-ray Photoemission Spectroscopic (XPS) Measurements: XPS measurements of the products were carried out on an ESCALAB 250 X-ray photoelectron spectrometer, at a pressure greater than 10^{-6} Pa. The general scan, C_{1s} , Te_{3d} and O_{1s} core level spectra were recorded with unmonochromated Al-K_α radiation (photon energy: 1486.6 eV). The core-level binding energies (BEs) were aligned with respect to the C 1s binding energy (BE) of 285 eV.

X-ray Diffraction (XRD) Measurements: The XRD of pattern was examined on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromated Cu-K_α radiation ($\lambda = 1.54178 \text{ \AA}$).

Raman Spectroscopic Studies: The Raman spectroscopic studies were performed with 488 nm laser excitation with a micro-Raman system which was modified by coupling an Olympus microscope to a Jobin-Yvon-HR800 spectrometer with a CCD detector.

Photoluminescence Spectroscopic Studies: Photoluminescence spectroscopy of the products was monitored with a F-4500 model photoluminescence spectrophotometer (Japan Hitachi Co.).

Supporting Information (see also the footnote on the first page of this article): Three figures showing XRD patterns FESEM images.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (NSFC) (20871089), the Key Project of Anhui Provincial Education Department (KJ2007A076) and the Scientific Research Foundation for the Professors (Doctors) of Suzhou University (2006jb03).

- [1] N. Petkov, J. Xu, M. A. Morris, J. D. Holmes, *J. Phys. Chem. C* **2008**, *112*, 7345–7355.
- [2] Y. Yan, L. Zhou, J. Zhang, H. Zeng, Y. Zhang, L. Zhang, *J. Phys. Chem. C* **2008**, *112*, 10412–10417.
- [3] L. I. Berger, *Semiconductor Materials*, CRC Press, Boca Raton, Florida, **1997**, pp. 86–88.
- [4] B. T. Mayers, K. Liu, D. Sunderland, Y. Xia, *Chem. Mater.* **2003**, *15*, 3852–3858.
- [5] J. Beauvais, R. A. Lessard, P. Galarneau, E. J. Knystautas, *Appl. Phys. Lett.* **1990**, *57*, 1354–1356.
- [6] a) M. S. Mo, J. H. Zeng, X. M. Liu, W. C. Yu, S. Zhang, Y. T. Qian, *Adv. Mater.* **2002**, *14*, 1658–1662; b) G. C. Xi, Y. Y. Peng, W. C. Yu, Y. T. Qian, *Cryst. Growth Des.* **2005**, *5*, 325–328; c) H. S. Qian, S. H. Yu, J. Y. Gong, L. B. Luo, L. F. Fei, *Langmuir* **2006**, *22*, 3830–3835.
- [7] a) B. Zhou, J. J. Zhu, *Nanotechnology* **2006**, *17*, 1763; b) Y. J. Zhu, W. W. Wang, R. J. Qi, X. L. Hu, *Angew. Chem. Int. Ed.* **2004**, *43*, 1410–1414.
- [8] a) X. L. Li, G. H. Cao, C. M. Feng, Y. D. Li, *J. Mater. Chem.* **2004**, *14*, 244–247; b) P. Mohanty, T. Kang, B. Kim, J. Park, *J. Phys. Chem. B* **2006**, *110*, 791–795; c) B. Geng, Y. Lin, X. Peng, G. Meng, L. Zhang, *Nanotechnology* **2003**, *14*, 983–986.
- [9] a) B. Mayers, Y. N. Xia, *Adv. Mater.* **2002**, *14*, 279–282; b) B. Mayers, Y. N. Xia, *J. Mater. Chem.* **2002**, *12*, 1875–1881.
- [10] a) J. M. Song, Y. Z. Lin, Y. J. Zhan, Y. C. Tian, G. Liu, S. H. Yu, *Cryst. Growth Des.* **2008**, *8*, 1902–1908; b) Z. B. He, S. H. Yu, *J. Phys. Chem. B* **2005**, *109*, 22740–22745; c) W. H. Xu, J. M. Song, L. Sun, J. L. Yang, W. P. Hu, Z. Y. Ji, S. H. Yu, *Small* **2008**, *4*, 888–893.
- [11] Q. Y. Lu, F. Gao, S. Komarneni, *Langmuir* **2005**, *21*, 6002–6005.
- [12] Z. Wang, L. Wang, H. Wang, *Cryst. Growth Des.* **2008**, *8*, 4415–4419.
- [13] J. F. Keggin, *Nature* **1933**, *131*, 908–909.
- [14] J. A. Huheey, *Inorganic Chemistry*, 3rd ed., Harper and Row, New York, **1983**, p. 698.
- [15] V. Kogan, Z. Izenshtat, R. Neumann, *Angew. Chem. Int. Ed.* **1999**, *38*, 3331–3334.
- [16] M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48.
- [17] A. Troupis, A. Hiskia, E. Papaconstantinou, *Angew. Chem. Int. Ed.* **2002**, *41*, 1911–1914.
- [18] S. Mandal, P. R. Selvakannan, R. Pasricha, M. Sastry, *J. Am. Chem. Soc.* **2003**, *125*, 8440–8441.

- [19] S. Mandal, A. B. Mandale, M. Sastry, *J. Mater. Chem.* **2004**, *14*, 2868–2871.
- [20] A. Sanyal, S. Mandal, M. Sastry, *Adv. Funct. Mater.* **2005**, *15*, 273–280.
- [21] S. Mandal, D. Rautaray, M. Sastry, *J. Mater. Chem.* **2003**, *13*, 3002–3005.
- [22] D. Rautaray, S. R. Sainkar, M. Sastry, *Langmuir* **2003**, *19*, 10095–10099.
- [23] S. Mandal, D. Rautaray, A. Sanyal, M. Sastry, *J. Phys. Chem. B* **2004**, *108*, 7126–7131.
- [24] L. Yang, Y. Shen, A. Xie, J. Liang, Sh. Li, Q. Zhang, *Eur. J. Inorg. Chem.* **2006**, 4658–4664.
- [25] L. Zhang, Y. H. Shen, A. J. Xie, S. K. Li, Y. M. Li, *J. Mater. Chem.* **2009**, *19*, 1884–1893.
- [26] A. Hiskia, A. Mylonas, E. Papaconstantinou, *Chem. Soc. Rev.* **2001**, *30*, 62–69.
- [27] I. A. Weinstock, *Chem. Rev.* **1998**, *98*, 113–170.
- [28] K. K. Caswell, C. M. Bender, C. J. Murphy, *Nano Lett.* **2003**, *3*, 667–669.
- [29] Z. H. Lin, Z. Yang, H. T. Chang, *Cryst. Growth Des.* **2008**, *8*, 351–357.

Received: February 11, 2009
Published Online: July 1, 2009