

# Controlled growth of multi-morphology hexagonal t-Se microcrystals: tubes, wires, and flowers by a convenient Lewis acid-assisted solvothermal method†

Dabin Yu,\* Tao Jiang, Feng Wang, Zirong Wang, Yan Wang, Wen Shi and Xiaoquan Sun

Received 6th November 2008, Accepted 4th February 2009

First published as an Advance Article on the web 3rd March 2009

DOI: 10.1039/b819852g

This paper reports on the controlled growth of multi-morphology hexagonal t-Se microcrystals by a convenient Lewis acid-assisted solvothermal method using the mixture of ethanol and H<sub>2</sub>O as solvent. The tubes and wires with a well-defined crystallographical structure and the flowers with chrysanthemum-, sisal-, and urchin-like shapes were obtained by changing Lewis acids and adjusting some other synthesis parameters, in particular the volume ratio of ethanol to H<sub>2</sub>O. Lewis acids were found to be crucial for the formation of the tubes and wires by not only acting as the PH regulator but also as the shape controller, owing to their hydrolysis in the solvent to *in situ* form H<sup>+</sup> and hydrates. The mixture of ethanol and H<sub>2</sub>O was responsible for the formation of various followers when NH<sub>4</sub>Cl was used instead of the Lewis acids with metallic ions. The findings suggested that this should be an effective approach to the controlled growth of t-Se crystals with interesting multiple morphologies, which are of interest for both theoretical investigations and practical applications.

## 1. Introduction

Controlled growth of architectural semiconductor micro- and nano-crystals with well-defined shapes has attracted significant attention over the past decade because the properties of the crystals depend not only on their compositions but also on their morphologies, structures, and sizes.<sup>1</sup> For example, tubes with several different areas of contact (borders, inner and outer surfaces, and structured tube walls) can be further functionalized in many ways, such as their usage as host materials;<sup>2</sup> wires with an exceptional 1D (1D) structure allow their applications as building blocks of structured assemblies, such as sensors;<sup>3</sup> flowerlike crystals with interesting dendritic shape have been, in recent years, considered as desired agents for understanding the growth mechanism and formation kinetics of crystals.<sup>4</sup> Up to now, although many methods, such as solvothermal process, chemical vapor deposition (CVD),<sup>5</sup> arc discharge,<sup>6</sup> laser ablation,<sup>7</sup> electrochemistry,<sup>8</sup> and templates,<sup>9</sup> etc., have been developed to control the growth of various micro- and nano-crystals, it is still an interesting and challenging issue to find more convenient methods for the controlled growth of micro- and nano-crystals.<sup>10</sup>

Trigonal selenium (t-Se), a p-type semiconductor with a band gap value of near 1.8 eV, has unique physical properties, such as anisotropy of the thermoconductivity, superconductivity, high photoconductivity, high piezoelectric, thermoelectric, and

nonlinear optical responses,<sup>11</sup> on the basis of which t-Se micro- and nano-crystals have been expected to have an even wider potential in many fields, such as solar cells, rectifiers, photographic exposure meters, and medical diagnostics.<sup>12</sup> The anisotropic crystal structure of t-Se contains covalently bonded Se atoms that are helically arranged in infinite chains bound together by Van der Waals attraction in the hexagonal lattice,<sup>13</sup> thus resulting in the fact that its micro- and nano-crystals always grow along one direction (the *c*-axis), which has been confirmed by the formation of its 1D micro-/nano-structures in the literature.<sup>14</sup> Up to now, t-Se micro-/nano-crystals, including rods, wires, tubes, and some dendritic crystals have been generated by several strategies.<sup>15</sup> Recently, Jeong's group have successfully observed the transformation process of amorphous Se (a-Se) into trigonal Se (t-Se) nanowires on solid substrates,<sup>16</sup> on the basis of the preparation of monodisperse a-Se colloids by reducing selenious acid with hydrazine hydrate.<sup>17</sup>

Herein, we report the controlled growth of multi-morphology hexagonal t-Se microcrystals, with a particular emphasis on the t-Se flowers, by a convenient Lewis acid-assisted solvothermal route using a mixture of ethanol and H<sub>2</sub>O as solvent. The as-synthesized t-Se crystals included various interesting shapes, such as tubes, wires, and flowers, all of which have, in fact, caused considerable research attention with regard to their controlled synthesis over the past decade, but they, to the best of our knowledge, have not been obtained using one method, so far.

## 2. Experimental

### Materials

Analytical grade Na<sub>2</sub>SeO<sub>3</sub>, chlorides (NH<sub>4</sub>Cl, MnCl<sub>2</sub>·4H<sub>2</sub>O, ZnCl<sub>2</sub>, AlCl<sub>3</sub>, FeCl<sub>3</sub>), N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, and ethanol were purchased from Shanghai Chemical Reagents Company and were used as received.

*State Key Laboratory of Pulsed Power Laser Technology, Electronic Engineering Institute, Huangshan Road, Hefei, Anhui, 230037, P. R. China. E-mail: dbyu@ustc.edu; Fax: +086-551-5767735; Tel: +086-551-5767735*

† Electronic supplementary information (ESI) available: Typical XRD patterns of other t-Se products; EDS spectra of various t-Se products; more SEM images of (A) tubes, (B) wires, (C) and (D) rods; more SEM images of the products with a critical shape between spheres and flowers; more SEM images of various t-Se flowers. See DOI: 10.1039/b819852g

### Growth of t-Se tubes and wires

In a typical synthesis procedure of Se microtubes, 30 mL of deionized water, 15 mL of ethanol, and 0.20 mL of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  were mixed in a Teflon-lined stainless steel autoclave of 55-mL capacity. 130 mg of  $\text{Na}_2\text{SeO}_3$  was then added into the autoclave, followed by the addition of 1 mmol of  $\text{AlCl}_3$  under vigorous stirring for *ca.* 5 min. The autoclave was sealed and heated at 130 °C in a furnace for 12 h. It was then allowed to cool naturally to room temperature. After that, the product was washed with water, 1 M HCl, water, and finally ethanol sequentially and was collected for further characterization. The synthesis process of wires was almost the same as that for the growth of Se tubes, but 1 mmol of  $\text{ZnCl}_2$  was used instead of 1 mmol of  $\text{AlCl}_3$ .

### “Planting of t-Se flowers”

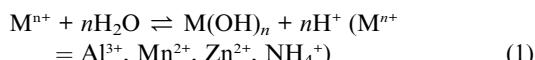
Typically, 20 mL of deionized water, 30mL of ethanol, and 0.20 mL of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  were mixed in a Teflon-lined stainless steel autoclave of 55-mL capacity. 173 mg of  $\text{Na}_2\text{SeO}_3$  and 0.2 mmol of  $\text{NH}_4\text{Cl}$  were then sequentially added into the autoclave under stirring. When the salts had dissolved, the autoclave was sealed and heated at 150 °C in a furnace for 12 h. A scarlet solution was obtained after the autoclave had been cooled to room temperature, and transferred into a 100-mL beaker. Aged under ambient conditions, the colour of the solution gradually became light, and a dark product was formed until the solvent became clear after *ca.* 3 h. After that, the product was washed with water and ethanol sequentially and was collected for further characterization.

### Characterization

The XRD patterns were recorded on a Philips X’Pert PRO-SUPER X-ray powder diffractometer ( $\lambda = 1.54178 \text{ \AA}$ ) in the  $2\theta$  range of 20–70°. The scanning electron microscopy (SEM) images and EDS spectra were taken on a Sirion 200 scanning electron microscope. The UV/vis absorption spectra were obtained on a U4100 spectrophotometer using a quartz cuvette with an optical path length of 1 cm at room temperature.

## 3. Results and discuss

Our synthesis scheme is based on the following chemical reactions:



The hydrolysis of the cations of Lewis acids resulted in the formation of two products, *i.e.*,  $\text{H}^+$  and hydrates (eqn (1)), the former acted as the pH adjuster that provided an acidic condition for the reduction of  $\text{SeO}_3^{2-}$  (eqn (2)), and the latter acted as shape controller in the solvent, resulting in an interesting shape-selective route to the formation of various t-Se crystals. It has been proved that a slightly acidic condition ( $\text{pH} < 7$ ) is favorable for the deoxidation of quadrivalent selenium, such as  $\text{SeO}_2$  and  $\text{SeO}_3^{2-}$ , to its nonvalent state,<sup>18</sup> due to the fact that the reduction

of  $\text{SeO}_3^{2-}$  can be approximately thought of as based on the following half-reaction with a standard potential of 0.74 V in the presence of  $\text{H}^+$  (eqn (3)).<sup>19</sup>



Obviously,  $\text{H}^+$  is one of the main factors that determine the reduction potential of  $\text{SeO}_3^{2-}/\text{Se}$ . With the reduction of  $\text{SeO}_3^{2-}$ ,  $\alpha$ -Se was produced under experimental conditions.<sup>18</sup> However,  $\alpha$ -Se is thermodynamically unstable and tends to transform into the much stabler t-Se,<sup>20</sup> during which the hydrates (except for  $\text{NH}_3 \cdot \text{H}_2\text{O}$  resulting from  $\text{NH}_4\text{Cl}$ ) further played a crucial role in the controlled growth of t-Se crystals. Therefore, Lewis acids played multiple roles in both the synthesis reactions and the crystal growth, which will further be discussed in the following sections.

Fig. 1 represents a typical XRD pattern of the t-Se tubes obtained under hydrothermal conditions by using ethanol/ $\text{H}_2\text{O}$  (v/v, 1 : 2) as solvent in the presence of  $\text{AlCl}_3$  at 130 °C. The diffraction pattern indicates that the product corresponds to the hexagonal phase Se (space group  $P3121$ ), *i.e.*, t-Se with lattice parameters of  $a = 0.4370 \text{ \AA}$  and  $c = 0.4951 \text{ \AA}$ , which are consistent with those in literature (PCPDF no. 6-0362), and also shows that the products are well crystallized and exhibit a pure phase with the removal of byproducts ( $\text{Al}(\text{OH})_3$ ) by HCl. It should be noted that the XRD pattern shows a remarkably strong peak of the (100) plane, indicating that the crystals have a very strong preferential tendency to grow along [001] (the  $c$ -axis). The crystal growth was largely confined to the  $c$ -axis allowing for the structures with very high aspect ratios, which should be attributed to the anisotropic crystal structure of t-Se with the helical chains of covalently bound Se atoms in the hexagonal lattice, thus resulting in the formation of such a kind of 1D shape. If other Lewis acids were used instead of  $\text{AlCl}_3$ , the products were still a pure phase of t-Se under the experimental conditions according to the XRD and EDS analysis (see Fig. S1 and Fig. S2†), but each product showed a different XRD pattern in view of the intensity of the diffraction peaks, indicating that the Lewis acids strongly affected the preferential growth property of the crystals, thus

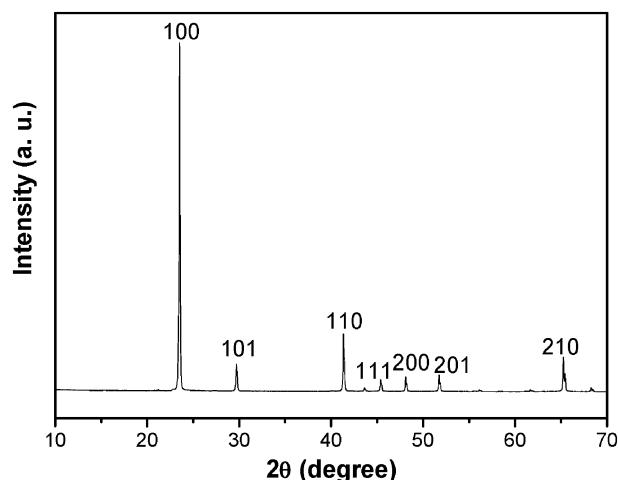
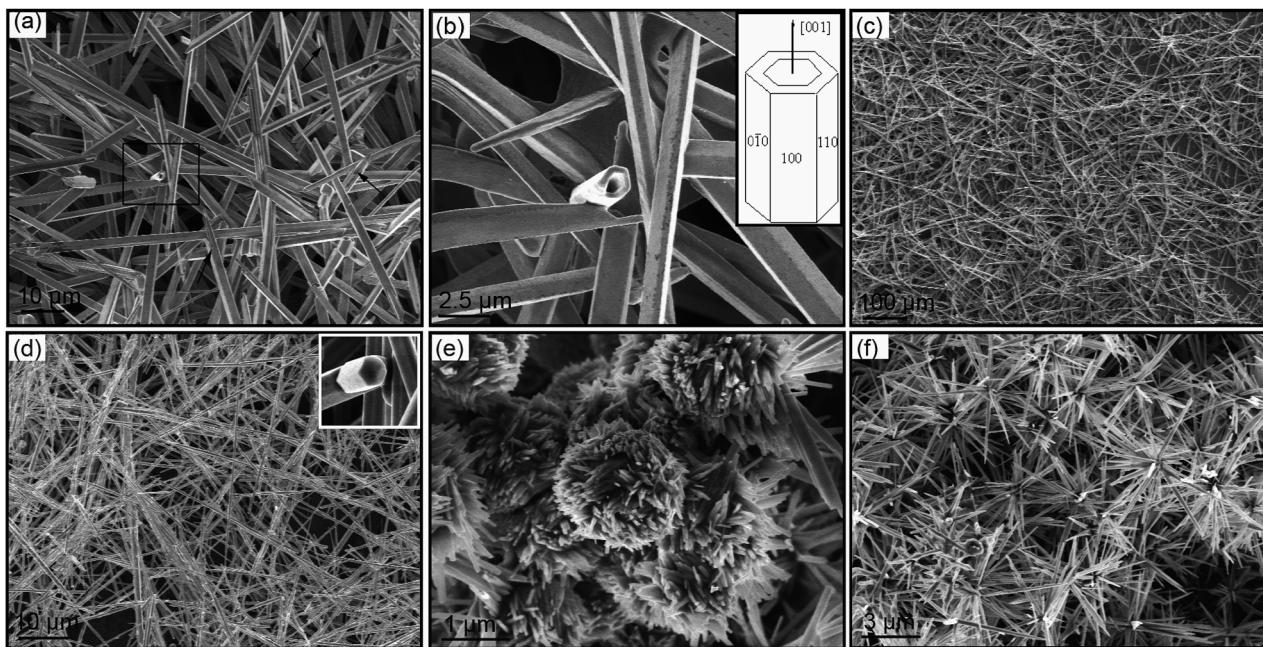


Fig. 1 A typical XRD pattern of t-Se tubes.

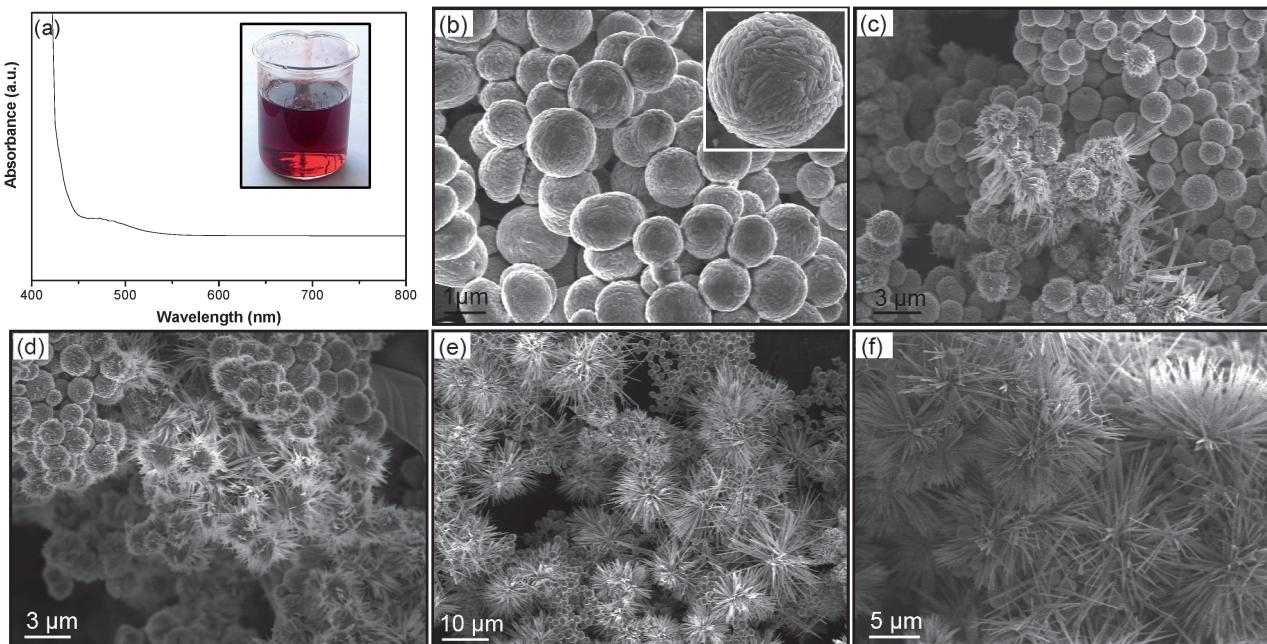
resulting in multiple shapes of the products, which can be further confirmed by SEM analysis.

Upon changing Lewis acids and some synthesis parameters, various t-Se crystals with interesting morphologies were synthesized as shown in Fig. 2. Fig. 2a shows a typical SEM image of the t-Se tubes as showed in Fig. 1. The product consisted of a large quantity of tubes with an average diameter of *ca.* 2.5 microns, wall thickness of *ca.* 300 nm, and length of up to tens of microns. In order to examine the shape of the tubes more clearly, a SEM image of Se tubes with higher magnifications, obtained from the area marked with a black pane in Fig. 2a, is exhibited as Fig. 2b. It can be seen that the tubes are of a well-defined crystallographic structure, *i.e.*, a hexagonal prism, the six facets of which are, most probably, bounded by six symmetric facets,  $(\bar{1}00)$ ,  $(010)$ ,  $(110)$ ,  $(100)$ ,  $(0\bar{1}0)$ , and  $(\bar{1}\bar{1}0)$ , as shown schematically in the inset of Fig. 2b, similar to the report in literature.<sup>15</sup> The preferential growth of the tubes was, therefore, along  $[001]$  direction, resulting in the strong preferential growth feature of the crystals, which was consistent with the XRD analysis. When the Lewis acids with divalent metal such as  $MnCl_2$  and  $ZnCl_2$  were used instead of  $AlCl_3$ , the products were long wires with diameter ranging from 1–3  $\mu$ m and length of up to hundreds of microns as shown in Fig. 2c and d. Similar to the tubes, most of wires (the inset of Fig. 2d) and rods (Fig. S3†) had a characteristic structure of hexagonal prism, which could also be attributed to the crystal nature of t-Se. When  $NH_4Cl$  was used instead of the Lewis acids as shown above, the products were mainly a series of flower-like crystals with interesting morphologies, such as chrysanthemum, sisal, urchin, *etc.*, which will be discussed in the next section.

An interesting result of this route should be the controlled growth of a series of t-Se flowers by using  $NH_4Cl$  instead of those Lewis acids with metallic ions. Different from the formation of t-Se tubes/wires which were carried out by a “one-pot” process, the flowers were formed by two steps, *i.e.*, a solvothermal reaction process and an aging growth process, which was similar to the growth of t-Se nanowires transformed from a-Se.<sup>16</sup> When the solvothermal reaction was completed in the autoclave, there appeared a kind of scarlet solution, which resulted from  $\alpha$ -Se colloids with a strong absorption in the range of 400–450 nm thus resulting in a red solution (Fig. 3a).<sup>18,20</sup> Because  $\alpha$ -Se colloids were thermodynamically unstable, they gradually transformed into t-Se crystals when the solution was aged under ambient conditions, during which various t-Se flowers were formed. Fig. 3b–f show an interesting “bloom process of Se flowers”, from buds to flowers. When the volume ratio of ethanol to  $H_2O$  was 1 : 1, t-Se spheres with average diameter of *ca.* 1.5  $\mu$ m were synthesized (Fig. 3b). It should be noted that each of the spheres was, in fact, the assembly of many small rod-like nanoparticles (inset in Fig. 3b), indicating that the small particles had a strong tendency to assemble in the synthesis process. Such an assembling tendency always made crystals a feature of dendritic growth.<sup>16</sup> With the concentration of  $Na_2SeO_3$  fixed at 20 mM, increasing the volume ratio of ethanol to  $H_2O$  led to a shape evolution of t-Se crystals from spheres to chrysanthemum-, sisal-, and urchin-like flowers. When the volume ratio was *ca.* 1.5 : 1, the crystals began to “bloom” (Fig. 3c). When the volume ratio was higher than 2 : 1, the crystals were dominated by flowers (Fig. 3d–f). It was interesting that the length of the branches of the dendritic crystals (“petals of the flowers”) increased



**Fig. 2** SEM images of various t-Se crystals synthesized under different conditions. (a) Tubes synthesized in the presence of  $AlCl_3$  at 120 °C. The black arrows indicate that the tubes have open ends. (b) Tubes with higher magnifications obtained from the area marked with a black pane as shown in Fig. 2a. The tubes clearly show a structure of hexagonal prisms. The inset illustrates the growth direction and the six facets of the individual tubes.<sup>15</sup> (c) Wires synthesized in the presence of  $ZnCl_2$  at 120 °C. (d) Wires synthesized in the presence of  $MnCl_2$  at 120 °C. The inset shows that the wires also have a structure of hexagonal prisms. (e)–(f) “Chrysanthemum” and “sisal” synthesized in the presence of  $NH_4Cl$  in different volume ratios of ethanol to  $H_2O$ .



**Fig. 3** (a) Photo and UV-vis absorption spectrum of the solution obtained by the solvothermal reaction at 150 °C. (b)–(f) SEM images of “bloom process of Se flowers” (from “buds” to “flowers”) synthesized in the presence of NH<sub>4</sub>Cl with different volume ratios of ethanol to H<sub>2</sub>O: (b) 1 : 1, (c) 1.5 : 1, (d) 2 : 1, (e) 3 : 1, (f) 4 : 1.

obviously with the increase of the ethanol : H<sub>2</sub>O volume ratio, and as a result, some chrysanthemum- and sisal-like crystals were formed.

As mentioned above, the shape-selective synthesis of t-Se crystals was attributed to the interesting combinations of various interdependent synthesis parameters similar to many reports for the controlled growth of various inorganic micro-/nano-crystals. First of all, among the synthesis parameters, Lewis acids played a crucial role in both the chemical reactions and the crystal growth, as shown above. In order to investigate the effect of Lewis acids on the synthesis, we have employed some Lewis alkalis, such as sodium acetate, instead of Lewis acids, and found that the oxidation–reduction reaction did not take place, which was due to the cathodic shift of the reduction potential of SeO<sub>3</sub><sup>2-</sup>/Se so that SeO<sub>3</sub><sup>2-</sup> could not be reduced by hydrazine hydrate under the experimental conditions. Meanwhile, we have also used some strong acids, such as HCl, instead of the Lewis acids, and found that although the chemical reactions could be carried out completely, the growth of t-Se crystal was uncontrollable, resulting in the formation of irregular crystals. Compared to the strong acids, Lewis acids provided much milder acidic conditions for the reduction of SeO<sub>3</sub><sup>2-</sup> because the hydrolysis of the cations was based on the reversible reaction (eqn (1)). In particular, hydrates were formed simultaneously with H<sup>+</sup> during the hydrolysis of the cations, and dispersed in the solvent in a jellied state due to their low solubility in the mixture of ethanol and H<sub>2</sub>O. As a result, once α-Se was produced, the hydrates acted as the host of α-Se and prevented it from generating multiple nuclei and randomly assembling into t-Se in the solvent. Therefore, t-Se crystals could grow in a controlled manner resulting in the formation of the 1D tubes and wires under the interaction of the intrinsic anisotropic feature of t-Se crystals and the control of

the hydrates. In addition, the metallic quantivalency in Lewis acids seemed to be related with the morphologies of the final products. For example, when the Lewis acids with a bivalent metal, such as ZnCl<sub>2</sub> and MnCl<sub>2</sub> were used, the main products were wires, when trivalent metallic chlorides, such as AlCl<sub>3</sub>, were used the products were predominated by tubes.

Solvent (ethanol/H<sub>2</sub>O) was found to be another important factor that determined the morphologies of t-Se crystals. In order to investigate the effect of solvents on the morphologies of the products, NH<sub>4</sub>Cl was used as the agent of Lewis acid so that there were no metallic hydrates formed in the hydrolysis reaction. As shown in Table 1, with the concentration of Na<sub>2</sub>SeO<sub>3</sub> and NH<sub>4</sub>Cl fixed at 20 and 5 mM, respectively, increasing the volume ratios of ethanol to H<sub>2</sub>O from 1 : 1 to 6 : 1 led to a shape evolution of t-Se crystals from spheres to “urchin, chrysanthemum, sisal”, and finally irregular dendritic crystals, meaning that solvent had a strong effect on the morphologies of the t-Se crystals. On the one hand, without the control of hydrates as described above, α-Se tended to generate multiple nuclei and randomly assemble in the solvent. Therefore, 1D growth tendency of t-Se crystals was weakened, compared to the growth of t-Se tubes in the presence of hydrates. On the other hand, varying the volume ratio of ethanol to H<sub>2</sub>O led to the change of the polarity of the solvents, which had a strong effect on the growth of t-Se crystals so that we could see the evolution of crystals from “buds to various flowers” when the volume ratio of ethanol to H<sub>2</sub>O was increased. In addition, the high-yield formation of various t-Se flowers indicated that the mixture of ethanol and H<sub>2</sub>O was favorable for the dendritic growth of t-Se crystals, which was also confirmed by some branched wires/tubes (Fig. S3†) resulting from the chemical connections between the nanowires.<sup>16</sup>

**Table 1** Various t-Se flowers synthesized under different conditions

Ethanol/ H <sub>2</sub> O (v/v) <sup>a</sup>	[Na <sub>2</sub> SeO <sub>3</sub> ] <sup>b</sup> / mM	[NH <sub>4</sub> Cl]/ mM	Temperature <sup>c</sup> /°C	Shape/profile <sup>d</sup>
1 : 1	20	5	150	Sphere
1.5 : 1	20	5	150	Sphere
2 : 1	20	5	150	Urchin
3 : 1	20	5	150	Chrysanthemum
4 : 1	20	5	15	Chrysanthemum
5 : 1	20	5	150	Sisal
6 : 1	20	5	150	Dendritic crystal
3 : 1	30	5	150	Chrysanthemum
3 : 1	40	5	150	Sphere
3 : 1	20	10	150	Chrysanthemum
3 : 1	20	20	150	Chrysanthemum
3 : 1	20	30	150	Sisal
3 : 1	20	5	<130	—
3 : 1	20	5	>160	Dendritic crystal

<sup>a</sup> The data were the volume ratios of ethanol to H<sub>2</sub>O in the solvent. <sup>b</sup> The initial concentrations of Na<sub>2</sub>SeO<sub>3</sub> and NH<sub>4</sub>Cl were approximately calculated according to the total volume of ethanol and H<sub>2</sub>O before mixing. <sup>c</sup> The temperature was the synthesis temperature during the hydrothermal process in the autoclave. <sup>d</sup> The product was dominated by the particles with such a shape.

In addition, some other synthesis parameters, including the concentrations of starting materials and chlorides, also had an effect on the morphologies of the crystals. For example, with the volume ratio of ethanol to H<sub>2</sub>O fixed at 3 : 1 (Table 1), when the concentration of Na<sub>2</sub>SeO<sub>3</sub> increased up to 40 mM, the product changed from flowers to spheres; when the volume ratio of ethanol to H<sub>2</sub>O and the concentration of Na<sub>2</sub>SeO<sub>3</sub> were kept constant, increasing the concentration of NH<sub>4</sub>Cl could also lead to some change of the shape of the crystals, but its effect was not very obvious, compared to that of other synthesis parameters. In addition, the desired temperature was in the range of 120 to 160 °C, which was favorable for the chemical reactions, the transition of a-Se, and the controlled growth of t-Se crystals.

## 4. Conclusions

We have demonstrated that multi-morphology hexagonal t-Se microcrystals including tubes, wires, and various flowers were synthesized in high yield by a convenient Lewis acid-assisted solvothermal route using ethanol/H<sub>2</sub>O as solvent. On the basis of hydrolysis reactions, Lewis acids acted as both the pH regulator for the synthesis reactions and the shape controller for the crystal growth of tubes and wires. Exceptionally, when NH<sub>4</sub>Cl was used

instead of other Lewis acids with metallic ions, various flowers were obtained by adjusting the volume ratios of ethanol to H<sub>2</sub>O. The results indicate that this method can be further extended to control the growth of versatile t-Se crystals, which may find application in many fields.

## References

- (a) Y. Cui and C. M. Lieber, *Science*, 2001, **291**, 851; (b) X. Wang, J. Zhuang and Y. D. Li, *Nature*, 2005, **437**, 121; (c) J. T. Han, Y. H. Huang, X. J. Wu, C. L. Wu, W. Wei, B. Peng, W. Huang and J. B. Goodenough, *Adv. Mater.*, 2006, **18**, 2145.
- (a) R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787–792; (b) M. S. Dresselhaus and H. Dai, *MRS Bull.*, 2004, **29**, 237–239.
- Z. Liu and P. C. Searson, *J. Phys. Chem. B*, 2006, **110**, 4318–4322.
- (a) B. Zhang, W. Dai, X. Ye, Z. Zuo and Y. Xie, *Angew. Chem., Int. Ed.*, 2006, **45**, 2571; (b) W. T. Yao, S. H. Yu, S. J. Liu, J. P. Chen, X. M. Liu and F. Q. Li, *J. Phys. Chem. B*, 2006, **110**, 11704–11710.
- (a) Y. Wu and P. Yang, *Chem. Mater.*, 2000, **12**, 605; (b) C. C. Chen and C. C. Yeh, *Adv. Mater.*, 2000, **12**, 738.
- S. Iijima, *Nature*, 1991, **354**, 56.
- A. M. Morales and C. M. Lieber, *Science*, 1998, **279**, 208.
- Y. W. Wang, L. D. Zhang, G. W. Meng, X. S. Peng, Y. X. Jin and Z. Zhang, *J. Phys. Chem. B*, 2002, **106**, 2502.
- Y. G. Guo, C. J. Li, L. J. Wan, D. M. Chen, C. R. Wang, C. L. Bai and Y. G. Wang, *Adv. Funct. Mater.*, 2003, **13**, 626.
- V. Schmidt and U. Gösele, *Science*, 2007, **316**, 698.
- (a) *Selenium*, ed. R. A. Zingaro and W. C. Cooper, Litton Educational Publishing, New York, 1974; pp 12–28 and 174–217; (b) L. I. Berger, *Semiconductor Materials*, CRC Press, Boca Raton, FL, 1997, p 86; (c) S. Y. Zhang, C. X. Fang, Y. P. Tian, K. R. Zhu, B. K. Jin, Y. H. Shen and J. X. Yang, *Cryst. Growth Des.*, 2006, **6**, 2809; (d) X. C. Jiang, B. Mayer, T. Herricks and Y. N. Xia, *Adv. Mater.*, 2003, **15**, 1740; (e) B. Gates, Y. Y. Wu, Y. D. Yin, P. D. Yang and Y. N. Xia, *J. Am. Chem. Soc.*, 2001, **123**, 11500.
- (a) B. D. Yao, Y. F. Chan and N. Wang, *Appl. Phys. Lett.*, 2002, **81**, 757; (b) M. H. Cao, X. L. Wu, X. Y. He and C. W. Hu, *Langmuir*, 2005, **21**, 6093.
- A. V. Hippel, *J. Chem. Phys.*, 1948, **16**, 372.
- (a) X. Liu, M. Mo, J. Meng and Y. T. Qian, *J. Cryst. Growth*, 2003, **259**, 144; (b) B. Gates, Y. Yin and Y. N. Xia, *J. Am. Chem. Soc.*, 2000, **122**, 12582; (c) B. Gates, B. Myers, A. Grossman and Y. N. Xia, *Adv. Mater.*, 2002, **14**, 1749.
- (a) U. K. Gautam, M. Nath and C. N. R. Rao, *J. Mater. Chem.*, 2003, **13**, 2845; (b) X. Li, Y. Li, W. Zhou, H. Chu, W. Chen, I. L. Li and Z. Tang, *Cryst. Growth Des.*, 2005, **5**, 911; (c) K. Tang, D. B. Yu, F. Wang and Z. Wang, *Cryst. Growth Des.*, 2006, **6**(9), 2160.
- S. Ko, G. D. Moon and U. Jeong, *Nanotechnology*, 2008, **19**, 345601.
- U. Jeong and Y. Xia, *Adv. Mater.*, 2005, **17**, 102.
- Q. Li and V. W.-W. Yam, *Chem. Commun.*, 2006, 1006–1008.
- Lange's Handbook of Chemistry* (eBook), 15th edn, ed. J. A. Dean, McGraw-Hill, Inc., New York, 1999; section 6.
- B. Mayers, B. Gates and Y. Xia, *Int. J. Nanotechnol.*, 2004, **1**, 86.