Large-Scale Synthesis of High Quality Trigonal Selenium Nanowires

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A direct and simple one-step hydrothermal reaction route has been developed for the synthesis of high quality trigonal selenium (t-Se) nanowires at 110 °C, with $(NH_4)_2S_2O_3$ and Na_2SeO_3 as starting materials in the presence of the surfactant sodium dodecyl sulfate (SDS). The diameter of the trigonal selenium nanowires can be tuned by carefully adjusting the initial feedstock concentration. The unusual chain like structure of the target material plays a key role in determining the final morphologies of the products. Several factors, such as initial concentration of the feedstock, the presence of surfactant, and the temperature which influences the quality of the t-Se nanowires, have been investigated. The optical properties of the t-Se nanowires with different diameters were examined by means of UV/Vis absorbance spectroscopy at room temperature. The investigation revealed that the absorbance peak for the t-Se nanowires with diameters of 20–40 nm shifts to the blue, relative to those for bulk t-Se nanowires (374 nm) and nanowires with diameters of 50–130 nm (306 nm).

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Introduction

Nanoscale one-dimensional (1D) materials, such as nanotubes, nanowires and nanorods, have stimulated great interest due to their importance in basic scientific research and potential technological applications.[1−3] Moreover, new synthetic methods for the synthesis of semiconductor 1D nanostructures, such as nanowires or quantum wires, and their potential use in applications ranging from integrated circuit interconnectors to functional electronic and optical devices, have recently been investigated.[4−7] Besides significant technological advances due to their unique electrical, optical, and mechanical properties, nanowires can provide a material system to experimentally test fundamental quantum mechanical concepts.

For many applications, nanowires must be crystalline and largely defect free, with diameters in the range of 10−100 nm and lengths that greatly exceed their diameters. Many semiconductor nanowires, including Si, Ge, GaN, GaAs, InP etc., have been explored using various methods, such as laser ablation, arc-discharge, vapor phase transport processes, chemical vapor deposition and template-based routes.[8−12] On the other hand, chemical approaches (so called bottom-up techniques) may provide a more promising technique for the preparation of 1D nanostructure materials, in terms of versatility and potential for large-scale production, than conventional methods. Recently, there has been a strong trend towards the application of solution synthesis techniques for the preparation of 1D materials.[13−16] The hydrothermal method is one of the promising solution synthesis routes for the exploration of novel materials, due to the relatively mild conditions required, the one-step synthetic procedure, and the fact that the particle size can be controlled.[17] We have selectively prepared semiconducting famatinite (Cu_3SbS_4) nanofibers and tetradrite ($Cu_{12}Sb_4S_{13}$) nanoflakes via the mild solution synthesis route.[18]

Selenium is an important group VI semiconductor, which has found applications in rectifiers, solar cells, photographic exposure meters, and xerography. It is also used in the glass industry to eliminate bubbles and remove undesirable tints produced by iron.[19] In addition, selenium also has a high reactivity towards numerous chemicals that can potentially be exploited to convert selenium into other functional materials such as CdSe, ZnSe, Ag_2Se etc.[20] It is reasonable to assume that the availability of 1D selenium nanowires will introduce new types of applications or enhance the performance of currently existing devices, as a result of size restriction. The acicular and filament single crystals of selenium were studied 40 years ago.[21,22] Recently, Xia and coworkers have exploited sonochemical irradiation, and self-seeding solution-phase processes for the preparation of trigonal selenium nanowires.[23,24] Zhang et al. prepared α-monoclinic selenium nanowires via the decomposition of selenodiglutathiones.[25] Abdelouas and co-workers have also attempted to employ a reduction reaction route using cytochrome c_3 for the synthesis of monoclinic Se

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nanowires.[26] More recently, Xie et al. reported a laser ablation method for the preparation of trigonal selenium nanorods at different temperatures.[27]

In this paper, we have designed a low-temperature hydrothermal synthesis route for the direct production of high quality crystalline trigonal selenium nanowires, using $(NH_4)_2S_2O_3$ and Na_2SeO_3 as starting materials in the presence of the surfactant sodium dodecyl sulfate (SDS). The initial concentration of feedstock solution is a key factor which influences the quality of the as-synthesized nanowires. The high yields of the products, without using complex apparatus, and the low reaction temperature employed, means that this simple method has good prospects for use in related future applications. The hydrothermal synthesis of t-Se nanowires is associated with the following chemical reaction.

$$(NH_4)_2S_2O_3 + Na_2SeO_3 \xrightarrow[110^{o}\,C]{SDS} Se + (NH_4)_2SO_3 + Na_2SO_3$$

In this process, the low solubility of selenium in water at 110 °C may be the driving force for this reaction to go to completion.

Results and Discussion

The obtained samples were weighed; the yields of the products were about 95%, based on the amount of Na_2SeO_3. Figure 1 (A) shows a typical XRD pattern of the sample prepared using 0.2 M feedstock in the presence of SDS at 110 °C for 18 h. All of the strong and sharp reflection peaks can readily be indexed to a single phase of trigonal-structured selenium (space group $P3_121$ (152) with infinite, helical chains of selenium atoms packed parallel to each other along the *c*-axis), with cell parameters a = 0.4364 nm and c = 0.4949 nm. These values are in agreement with the values reported in the literature (JCPDS Cards No. 73−0465). The product formed is further confirmed by XPS and Raman spectroscopy. Figure 1 (B) shows the XPS of the as-synthesized product. The binding energy at 54.8 eV, corresponding to Se3d, is the characteristic peak for elemental selenium.[28] Figure 1 (C) presents the Raman spectrum of the sample. The resonance peak at 237 cm^{-1} is a characteristic signature of trigonal selenium, which can be assigned to the vibration of the Se helical chain.[23] In comparison, the characteristic Raman peaks for monoclinic selenium and α-Se are at 256 cm^{-1} and 264 cm^{-1}, respectively.[29] These results, obtained from XRD, XPS and Raman spectroscopy, indicate that phase-pure t-Se is successfully produced via the present one-step synthetic route.

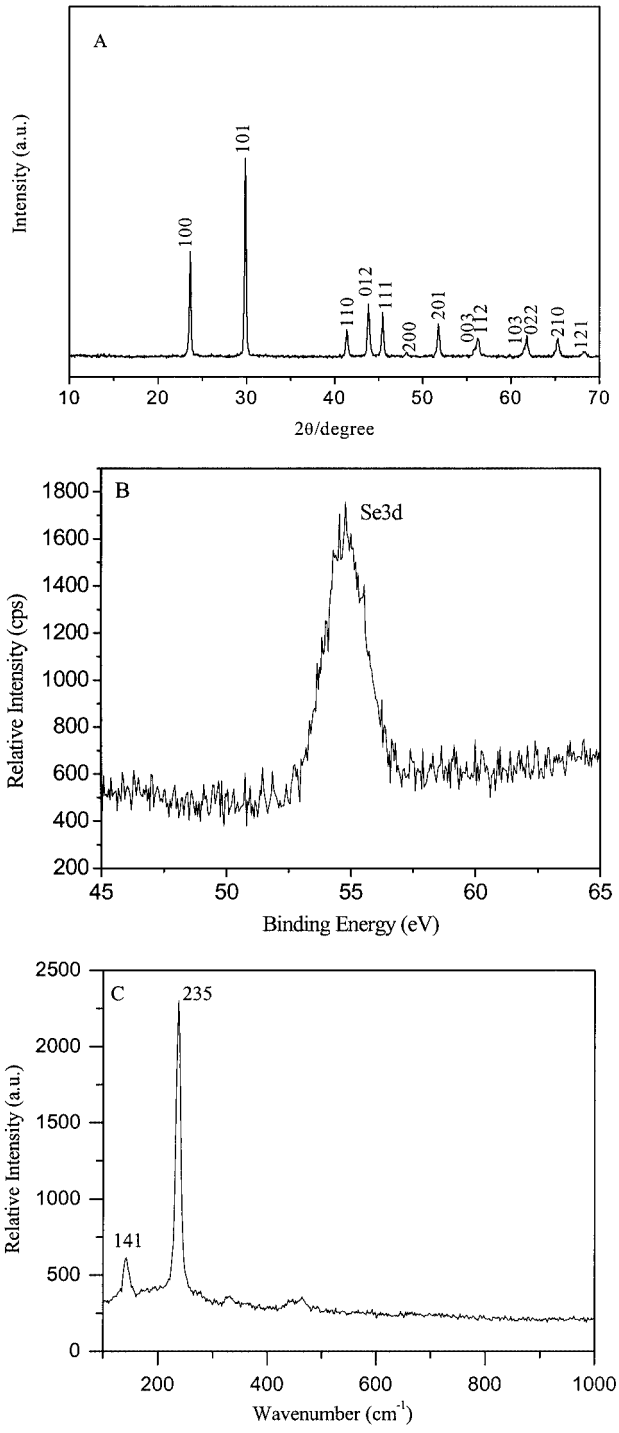

Figure 1. (A) Typical XRD pattern of the sample with 0.2 M feedstock solution in the presence of SDS; (B) XPS spectrum of the same sample as used in A; (C) Raman spectrum of the same sample as used in A

Figure 2 (A−C) provide SEM and TEM images of the same product as that presented in Figure 1. These images clearly show that the sample obtained is composed of a large number of nanowires, with a high aspect ratio (length/diameter). The uniformity in lateral dimension, the level of perfection, and the copiousness in quantity, show a good growth environment for the selenium nanowires in our system. Their lengths range from several micrometers to tens of micrometers, and their diameters are 20−40 nm, which is in agreement with that of micelles formed by SDS in aqueous solution.[30] The aspect ratio of the nanowires is in the range of several hundreds, which may be a useful feature in related applications. The inset of Figure 2 (C) shows the

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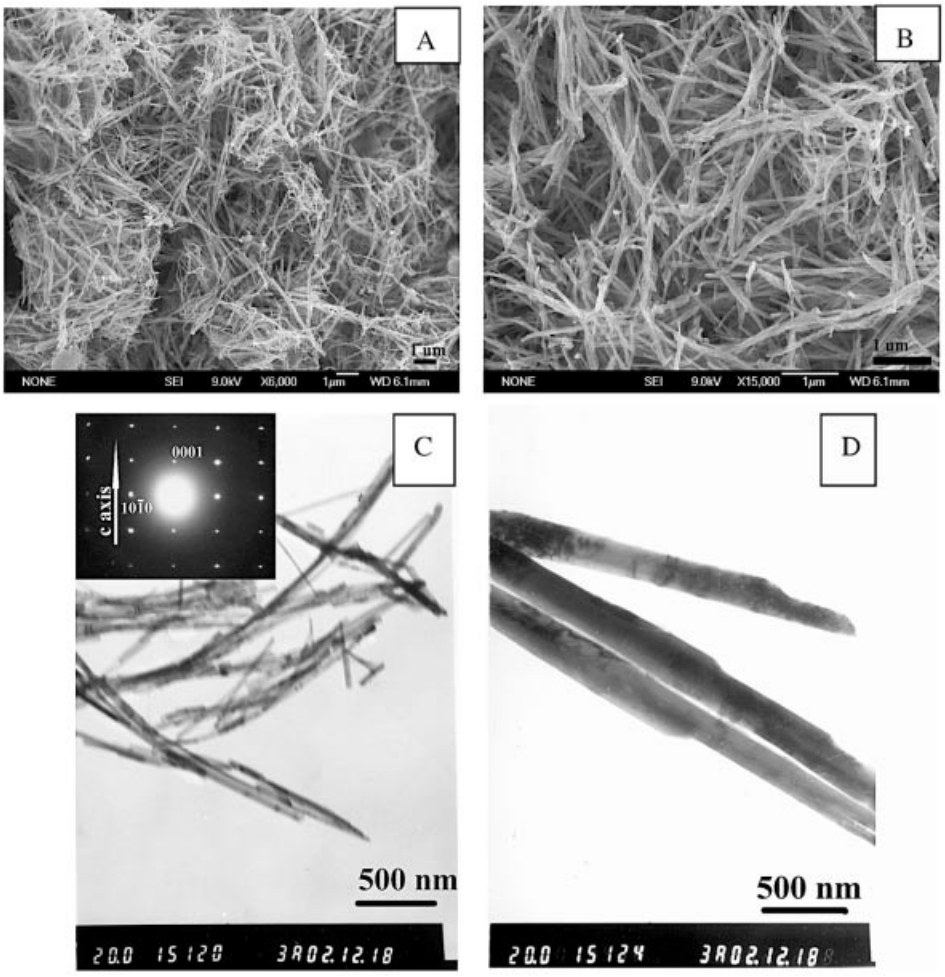

Figure 2. (A−B) Low and high magnification of the SEM images of the t-Se nanowires with 0.2 M feedstock solution in the presence of SDS; (C) TEM image of the same sample as presented in Figure 1A and ED pattern from a single nanowire (inset); (D) TEM image of the sample prepared with 0.1 M feedstock solution in the presence of SDS

selected-area electron diffraction (SAED) pattern obtained from a single nanowire, and exhibits the single-crystalline nature of nanowires. The two-fold rotational symmetry associated with this pattern indicates that these t-Se nanowires had predominately grown along the [001] direction (*c*-axis), with the helical chains of the Se atoms parallel to the longitudinal axis.[31] We have also carried out extensive investigations on more individual nanowires using ED, the results of which demonstrate that the as-synthesized sample is single-crystalline.

Selenium nanowires with larger diameters can be obtained when the initial concentration of the feedstock is reduced. Figure 2 (D) is a TEM image of the sample prepared with 0.1 M feedstock solution, whilst keeping the other conditions identical to those in the synthesis of the sample presented in Figure 1. It can be seen that the diameter (50−300 nm) of this product is much larger than that of the product synthesized at high initial concentrations. The length of the nanostructures is in the range of 2−5 μm. The corresponding aspect ratio ranges from 40 to 100. The experimental results demonstrate that the lateral dimensions of the products are strongly dependent on the initial concentrations of the feedstock. Such a dependence can be employed to control the lateral dimensions of the nanowires in the range of 20−300 nm. There have been some similar reports that show that increasing the initial concentration of reagents will favor the formation of 1D nanostructures with a high aspect ratio. Alivisatos and co-workers have systematically studied the conditions for the shape-controlled growth of CdSe nanocrystals in a mixed hexylphosphonic acid (HPA) and trioctylphosphane oxide (TOPO) surfactant system. Their results indicated that as the monomer concentration is increased, the average aspect ratio of the CdSe nanorods increase rapidly.[32] Whilst preparing Te nanorods in a sodium dodecyl benzenesulfate (NaDDBS) surfactant system, Liu et al.[33] also found that on increasing the initial concentration of $(NH_4)_2TeS_4$, the diameter of the 1D nanostructures decrease, and the nanowires will favorably be formed when a high concentration of $(NH_4)_2TeS_4$ is used. The observed phenomena in our experiments can be explained according to the previous reports.[32] At a given temperature, the high reagent concentration can provide enough selenium nuclei seeds, with a relatively narrow size distribution as the starting point. The

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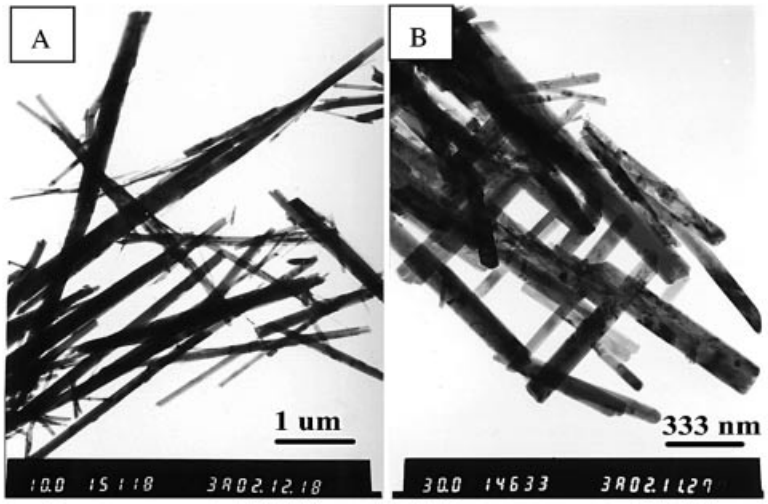

Figure 3. TEM images of the products obtained with different initial concentrations of feedstock solution in the absence of SDS (A) 0.2 M (B) 0.1 M

growth of the particles will be along the unique *c*-axis of t-Se, and finally results in high quality nanowires.

In contrast, we also prepared samples in the absence of surfactant, whilst keeping the other conditions constant. As shown in Figure 3, the TEM image of the sample synthesized using 0.2 M feedstock without using the surfactant displays uniform nanorods with diameters of 50−120 nm and lengths of up to 5 μm. When the concentration is decreased to 0.1 M, the diameters of the obtained sample are found to be 35−130 nm with lengths of about 2 μm [Figure 3 (B)]. The concentration-dependence of the diameter in the absence of surfactant is much less pronounced than that in the presence of surfactant. Hence, the surfactant is an important factor for the formation of high quality t-Se nanowires.

UV/Vis absorbance spectroscopy was used to characterize the samples. Figure 4 (A−C) shows the absorbance spectra of the obtained trigonal selenium nanowires with mean diameters of 20−40 nm, 50−120 nm and bulk t-Se, respectively. The results show that the absorbance peak for the t-Se nanowires with diameters of 20−40 nm (285 nm) is shifted to the blue, relative to those of the nanowires with diameters of 50−130 nm (306 nm) and bulk t-Se nanowires (374 nm). This shift can be attributed to the smaller diameters and larger aspect ratios of the nanowires.[34,35] Moreover, it should be noted that there is a large blue shift for both nanowires relative to that for the reported Se nanoparticles (620 nm).[19] As already known, different preparation methods have important effects on material microstructure and physical properties.[36] We believe that the optical properties of t-Se nanoparticles might be associated with its morphology and size. Thus, different optical characteristics are seen for t-Se nanowires and nanoparticles. Of course, our present understanding of the optical mechanism of crystalline t-Se nanoparticles is still limited, and more in-depth studies are underway.

Using the soft solution process, one-dimensional trigonal selenium nanostructures (nanowires or nanorods) have successfully been obtained, regardless of whether surfactants are used. In this solution-solid transformation, the morphology of the final product is determined mainly by the anisotropic nature of the target material. In other words, the 1D characteristic of the infinite, helical chains of selenium in the trigonal phase provides a natural template to define and guide the growth along one particular axis (*c*-axis). However, SDS and a relatively high initial concentration of feedstock solution are important factors for the formation of high quality trigonal selenium nanowires. The surfactant may act as a "size-tunable" reagent for the formation of selenium nanowires. A similar observation was reported for the preparation of γ-Al_2O_3 nanofibers with poly(ethylene oxide) as the surfactant.[37] We have also investigated the effect of temperature on the formation of t-Se nanowires. When the temperature is below 100 °C, the reaction is very slow and does not go to completion, and the yield is very low. When the temperature is above 130 °C, the size of the products is larger. Figure 5 shows a TEM image of the sample obtained at 150 °C using 0.2 M feedstock solution in the presence of SDS. It can be seen that the diameter of the rod-like crystal is up to 500 nm. This phenomena can be attributed to deterioration with increase in hydrothermal temperature. Therefore, 110 °C was chosen as the optimum temperature for the hydrothermal synthesis of t-Se nanowires.

Conclusion

A simple and convenient hydrothermal reaction route has been developed for the synthesis of high quality trigonal selenium nanowires in the presence of SDS. Several factors such as initial concentration of the feedstock, the presence of surfactant, and the temperature which influences the quality of the t-Se nanowires have been investigated. The unusual anisotropic structure of trigonal selenium provides a natural template to determine the morphology of the final products. The present route may be extended to the direct

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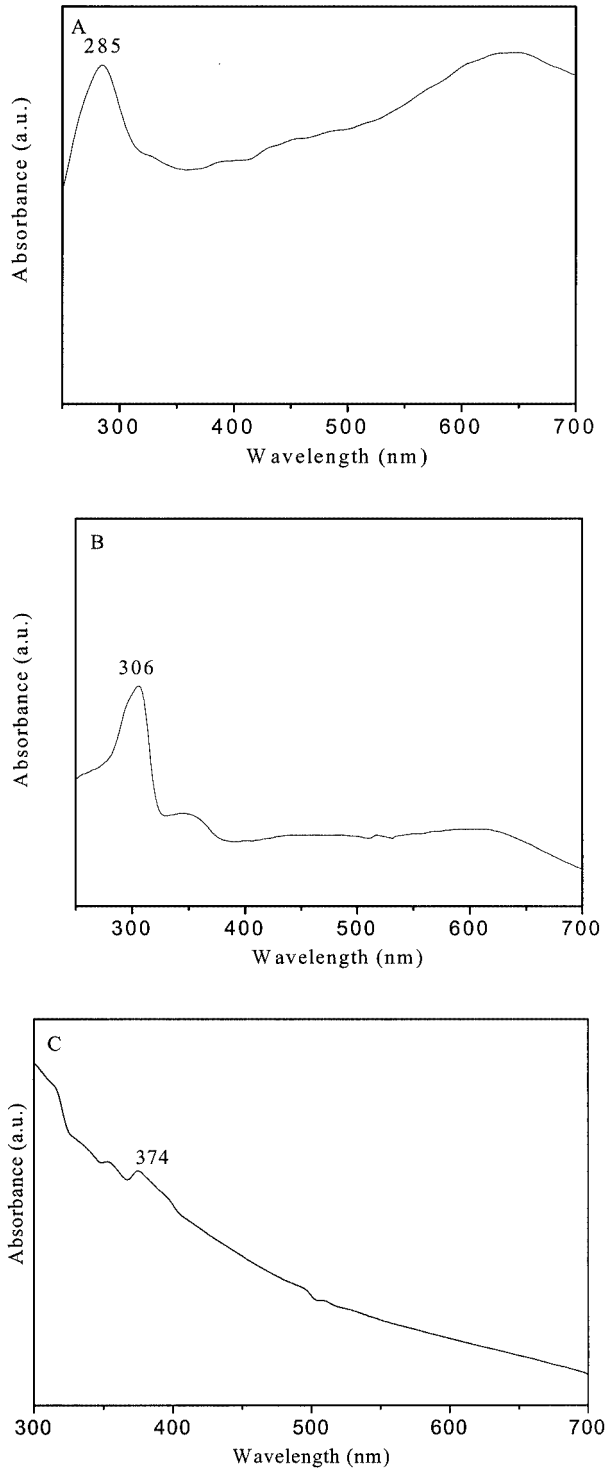

Figure 4. UV/Vis absorbance spectra of t-Se nanowires with different diameters (A) 20−40 nm; (B) 50−120 nm; (C) bulk t-Se

synthesis of 1D selenides. Moreover, the as-synthesized selenium nanowires may be useful in providing templates for the formation of 1D nanostructures of many technologically important materials, by reacting with other chemicals. The related studies are in progress and will be reported later.

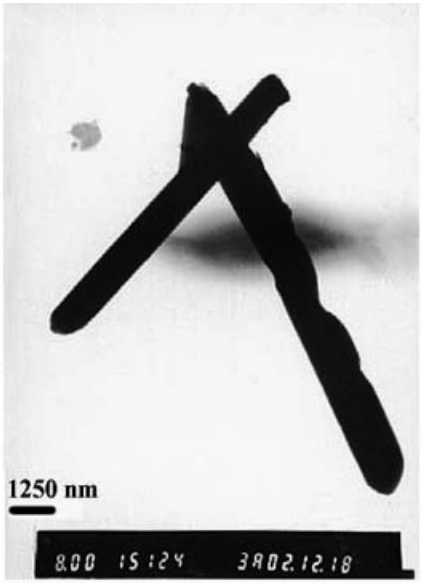

Figure 5. TEM image of the sample obtained at 150 °C

Experimental Section

All chemical reagents in this work, such as $NH_4S_2O_3$, Na_2SeO_3 and sodium dodecyl sulfate (SDS), were of A.R. grade and purchased from Shanghai Chemical Company, China. They were used as received without further purification.

Preparation of High Quality t-Se Nanowires

In a typical procedure, equivalent molar amounts of $(NH_4)_2S_2O_3$ and Na_2SeO_3 (10 mmol) were added to an aqueous solution (50 mL) of SDS (0.325 g). The solution was stirred for approximately 20 min until the solids had completely dissolved, and a 0.2 M homogeneous solution was formed. The solution was then transferred to a Teflon-lined autoclave (capacity of 60 mL). The autoclave was sealed and heated at 110 °C for 16−18 h, after which the autoclave was allowed to cool to room temperature naturally over a period of about 5 h. The resulting precipitate was rinsed with distilled water and absolute alcohol several times. After drying in vacuo at 40 °C for 4 h, the orange-red powders were collected for characterization.

For comparison, we prepared samples in the absence of surfactant whilst keeping the other conditions identical to those used in the preparation of high quality t-Se nanowires. Moreover, studies on the effect of initial concentrations (0.2 M, and 0.1 M) of feedstock solution on the resulting products were also carried out. The detailed experimental conditions were also similar to those used in the synthesis of high quality t-Se nanowires, with the exception that the initial feedstock concentrations were varied.

Sample Characterization

The phase composition and structure of the as-synthesized products were examined by X-ray powder diffraction (XRD), operating on a Japan Dmax-γA X-ray diffractometer with graphite-monochromated Cu-K_α radiation (λ = 1.54178 Å). X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromated Mg-K_α radiation as the excitation source. The Raman spectra were recorded on a Jobin Yvon HR800 (Horiba group), using 514.5 nm as the excitation line. The morphology and particle size of the final

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products were determined by scanning electron microscopy (SEM), using a JEOL-6700F scanning electron microanalyzer, and Transmission electron microscopy (TEM), using a Hitachi H-800 transmission electron microscope with a tungsten filament and an accelerating voltage of 200 KV. Room temperature absorbance spectra were recorded on a Shimadzu UV/Vis absorbance diode array spectrometer, using 1 cm quartz cuvettes. The samples were prepared by dispersing t-Se nanowires in absolute alcohol.

Acknowledgments

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