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RESEARCH ARTICLE

Rapid growth of t-Se nanowires in acetone at room temperature and their photoelectrical properties

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Abstract Trigonal selenium (t-Se) nanowires with uniform sizes were obtained through the conversion from freshly prepared amorphous selenium (a-Se) nanoparticles in acetone at room temperature. The experimental results show that some organic solvents, such as acetone and pyridine can dramatically promote the conversion from a-Se to t-Se, and t-Se with different morphologies like nanowires and microrods can be obtained. Acetone is an appropriate medium for obtaining t-Se nanowires in a short time. The as-prepared t-Se nanowires were characterized and confirmed by means of powder X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM). The photoelectrical properties of t-Se nanowires were investigated, which shows their potential uses in the fabrication of microdevices or photo-switches.

Keywords trigonal selenium, nanowires, photoelectrical properties

1 Introduction

As an important elemental semiconductor, selenium has been widely used in photocells, photographic exposure meters, xerography, pressure sensors and electrical rectifier due to its high photoconductivity, excellent spectral sensitivity and large piezoelectric, thermoelectric and nonlinear responses [1–4]. In addition, due to its high reactivity toward a wealth of chemicals, selenium with special morphology can serve as templates to be transformed into many other important functional materials, such as AgSe [5], ZnSe [6] and $CdSe_xTe_{1-x}$ [7].

Among the different allotropic forms of selenium, trigonal selenium (t-Se) is the most stable allotropic form. It contains infinite helical Se_n chain conformation along the *c*-axis. The other less stable allotropic forms of Se, such as amorphous selenium (a-Se) and monoclinic Se (m-Se), can be converted into more stable t-Se. Considerable efforts have been devoted to generating t-Se nanorods, nanowires, nanobelts, and nanowire networks by employing techniques such as laser ablation [8], sonochemical approaches [9], solution-mediated transformations [10], refluxing [11], hydrothermal methods [12], chemical vapor deposition (CVD) [13], and biomolecule assisted methods [14].

As for the solution-phase synthesis of t-Se nanomaterials, the initial selenium generated from reducing selenium-containing compounds is a-Se, so the transformation of a-Se into t-Se is an important step. Many factors, such as temperature, light, and ultrasonic can obviously affect the conversion from a-Se to t-Se. For example, Xia et al. found that ultrasonic can speed up the conversion from a-Se nanoparticles to t-Se nanowires [15]. Xie et al. prepared t-Se micromaterials with tubular, rod-like, and shuttle-like morphologies and nanotubes using a photothermally assisted solution phase approach. In their study, they found that visible light can promote the conversion from a-Se to t-Se [16].

In the present work, we find that some organic solvents, such as acetone and pyridine can dramatically promote the conversion from a-Se to t-Se. The conversion from a-Se to t-Se can be completed in several seconds or several hours at room temperature depending on the type of solvent, and the obtained t-Se have morphologies of nanowires or microrods. Among the organic solvents, acetone is an appropriate solvent for the rapid growth of t-Se nanowires from a-Se nanoparticles. This method for the preparation of t-Se nanowires is simple and convenient, and do not need any complicated apparatus. The photoelectrical properties of t-Se nanowires and a-Se nanoparticles were investigated. The t-Se nanowires show better photoelectrical properties than that of the a-Se nanoparticles, while t-Se nanowires have better stability. This result shows that

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t-Se nanowires are a better candidate for photoelectrical applications.

2 Experimental section

2.1 Preparation of a-Se

Na_2SeSO_3 solution was first prepared according to a previous report [17], as summarized in the following: 3.95 g selenium powder was added to 50 mL 1.0 M Na_2SO_3 solution. The solution was heated with a water bath to 90°C for about an hour under continuous magnetic stirring. After that, the unreacted selenium powder was filtered off and the Na_2SeSO_3 solution was collected for further use.

In a typical procedure, 2 mL Na_2SeSO_3 solution was added to 15 mL distilled water, then 4 mL 1.0 M HCl solution was added. Brick red a-Se precipitates appeared immediately. The precipitates were collected by centrifugation, washed with distilled water and absolute ethanol for several times, and then collected for further use.

2.2 Synthesis of t-Se nanowires

The freshly prepared a-Se precipitates were dispersed in 20 mL acetone by stirring. Then the solution was stored in dark. After the precipitates were changed from brick red to dark red, they were collected for identification and characterization.

2.3 Characterization

X-ray powder diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 0.15406 nm). Raman spectrum was investigated with a Labram-HR confocal laser micro-Raman spectrometer equipped with an argon ion laser with the excitation of 514.5 nm. The scanning electron microscope (SEM) images were taken with a Hitachi S-4800 scanning electron microscope. The high-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) patterns were recorded on a JEOL-2011 high-resolution transmission electron microscope performed at an acceleration voltage of 200 kV. The electrical measurements were tracked with a CHI 620B electrochemical workstation in a cell containing 20.0 mL 0.5 M HCl at room temperature using an Ag/AgCl electrode and a platinum wire as the reference electrode and the counter electrode, respectively.

3 Results and discussion

The composition and phase of the as-obtained sample were examined by XRD. Figure 1(a) shows the XRD pattern of the prepared t-Se sample. All of the diffraction peaks in this pattern can be readily indexed to the trigonal phase of Se, the lattice constants calculated from this pattern are a = 0.4362 nm and c = 0.4941 nm, which are in good agreement with the reported values of a = 0.4366 nm and c = 0.4953 nm (JCPDS Card No. 6-362). Compared with the standard pattern of t-Se, it is found that in Fig. 1(a) the intensity of (hk0) reflection peaks is abnormally strong, which suggests that the as-obtained t-Se crystals have a preferential growth orientation of [001].

The Raman spectrum further confirms the trigonal phase

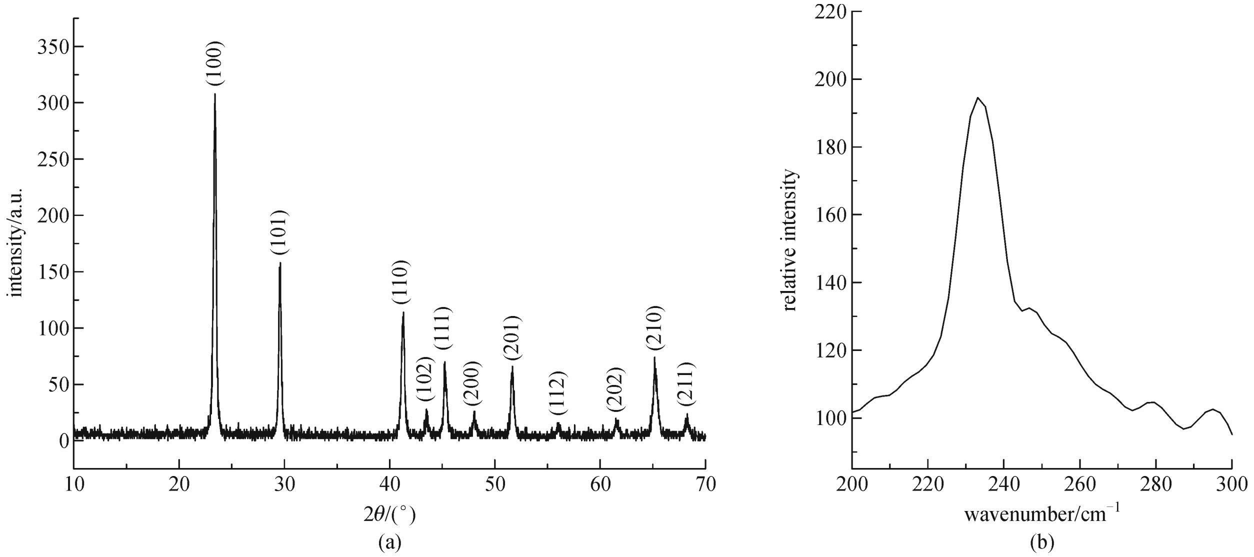


Fig. 1 (a) XRD pattern of the prepared t-Se nanowires; (b) Raman scattering spectrum of the Se nanowires corresponding to trigonal phase of Se

of Se. Figure 1(b) shows a typical Raman spectrum of the prepared sample. Only one strong Raman resonance peak at around 233 cm^{-1} was observed. This peak can be attributed to the vibration of helical selenium that exists only in the trigonal phase of Se [18–20]. No peaks for monoclinic Se (256 cm^{-1}) and a-Se (264 cm^{-1}) can be observed, which indicates that the as-prepared Se has high purity in phase [21].

The morphology and dimension of the as-prepared sample were examined by SEM, TEM and HRTEM. Figure 2(a) shows a typical SEM image of the sample, in which a large number of nanowires with lengths of several tens of micrometers can be observed. A clear view of the t-Se nanowires in Fig. 2(b) demonstrates that the nanowires have smooth surfaces, with average diameters of about 150 nm. Figure 2(c) shows a TEM image of the Se nanowires, further confirming the wire-like morphology with high degree of crystallinity. The diameters of these nanowires are about 150 nm, consistent with the SEM observations. The HRTEM image in Fig. 2(d) shows the single crystal nature of the nanowires. The observed interplanar spacings along and perpendicular to the growth direction are 0.496 nm and 0.378 nm respectively, which corresponds to the separation between (001) and (100) lattice planes of t-Se, respectively. The SAED pattern of this nanowire shown as an inset in Fig. 2(d) can be indexed to the $[0\bar{1}0]$ zone axis of t-Se, which also suggests that this nanowire grows along the [001] direction. This result is consistent with the XRD analysis.

A series of experiments were conducted to study the conversion from a-Se to t-Se in different solvents at room temperature, the results are summarized in Table 1. The prepared a-Se is red-brick. The SEM observation as shown in Fig. 3(a) indicates that the a-Se sample is composed of many irregular nanoparticles with diameters of about 300 nm. When the a-Se sample was dispersed in distilled

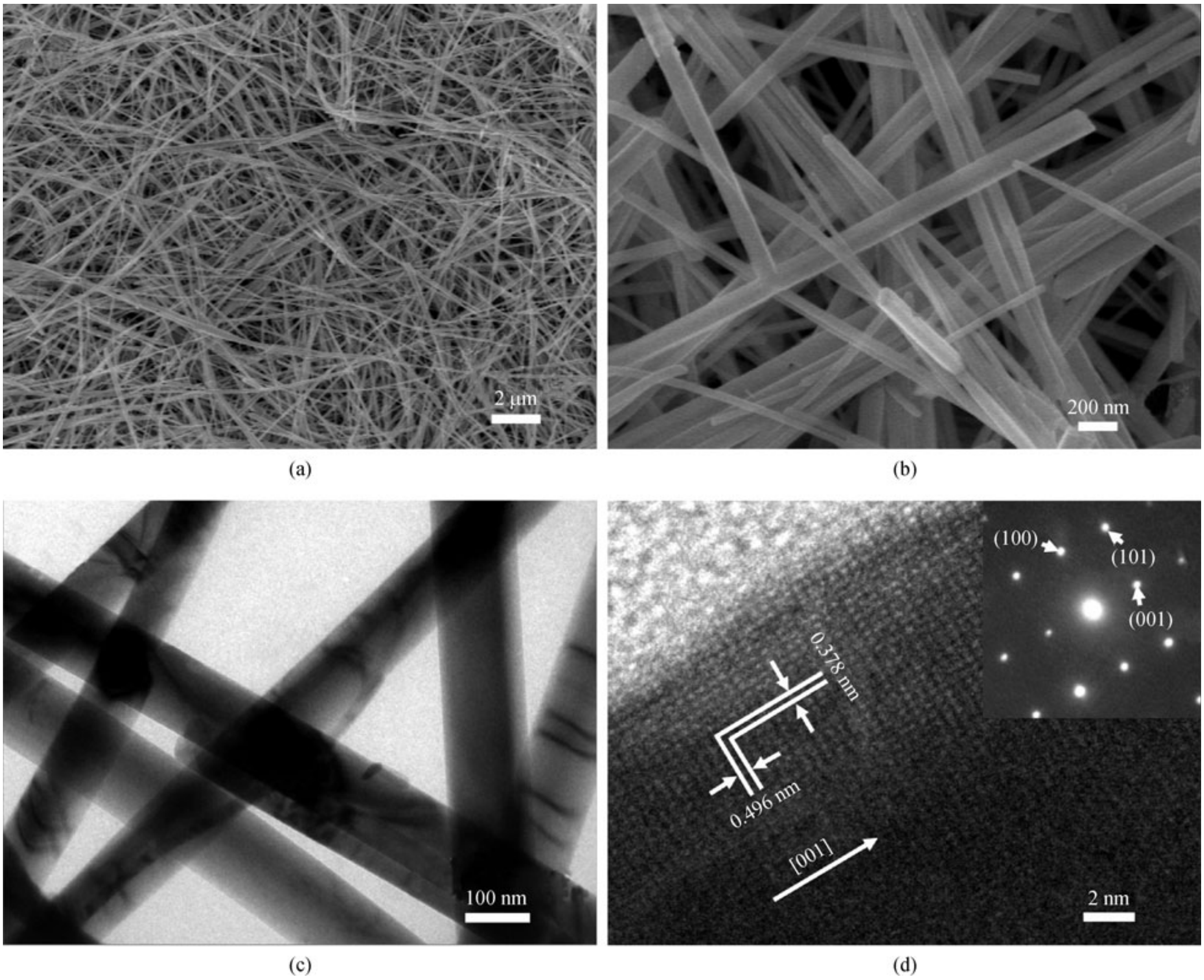


Fig. 2 (a), (b) SEM images of t-Se nanowires; (c) TEM image of t-Se nanowires; (d) HRTEM image of the t-Se nanowires, inset shows the corresponding SAED pattern

Table 1 Effect of different solvents on conversion from a-Se to t-Se

sovent	conversion time	product morphology	product color
water	–	–	–
acetonitrile	one week	nanowires	dark red
ethanol	one day	nanowires	dark red
acetone	two hours	nanowires	dark red
pyridine	less than five seconds	microrods	black
ethylenediamine	less than five seconds	microrods	black

water, no color change can be observed even after one month. The SEM analysis shows that no morphology change occurred. This result indicates that a-Se is hard to be converted into t-Se in water at room temperature. However, the conversion from a-Se to t-Se can be achieved in some organic solvents at room temperature, and in different solvents, the conversion time is distinctly different and the morphology of the prepared t-Se is also different. When the a-Se nanoparticles were dispersed in acetonitrile, the color of the sample gradually changed from brick red to dark red after about 1 week, indicating the transformation from a-Se to t-Se. The SEM image of the obtained sample is shown in Fig. 3(b). The sample is composed of many nanowires with an average diameter of about 80 nm. When ethanol instead of acetonitrile was used, the conversion from a-Se nanoparticles to t-Se nanowires can be completed in about 1 day. The SEM image in Fig. 3(c) of the prepared sample shows many nanowires with an average diameter of about 120 nm. If acetone was used as the solvent, t-Se nanowires can be obtained in a much shorter time, 2 h, and the obtained t-Se nanowires have an average diameter of about 150 nm as shown in Fig. 3(d). When pyridine was used as the solvent, the color of the sample changes from brick red to black in a very short time (less than 5 seconds), indicating a fast conversion speed. The SEM image in Fig. 3(e) indicates that many short microrods with an average diameter of about 600 nm and a length of about 1200 nm are obtained. The difference of the color between t-Se samples may be due to their different sizes. When ethylenediamine was used as the solvent, the result is similar to that of pyridine, as shown in Fig. 3(f).

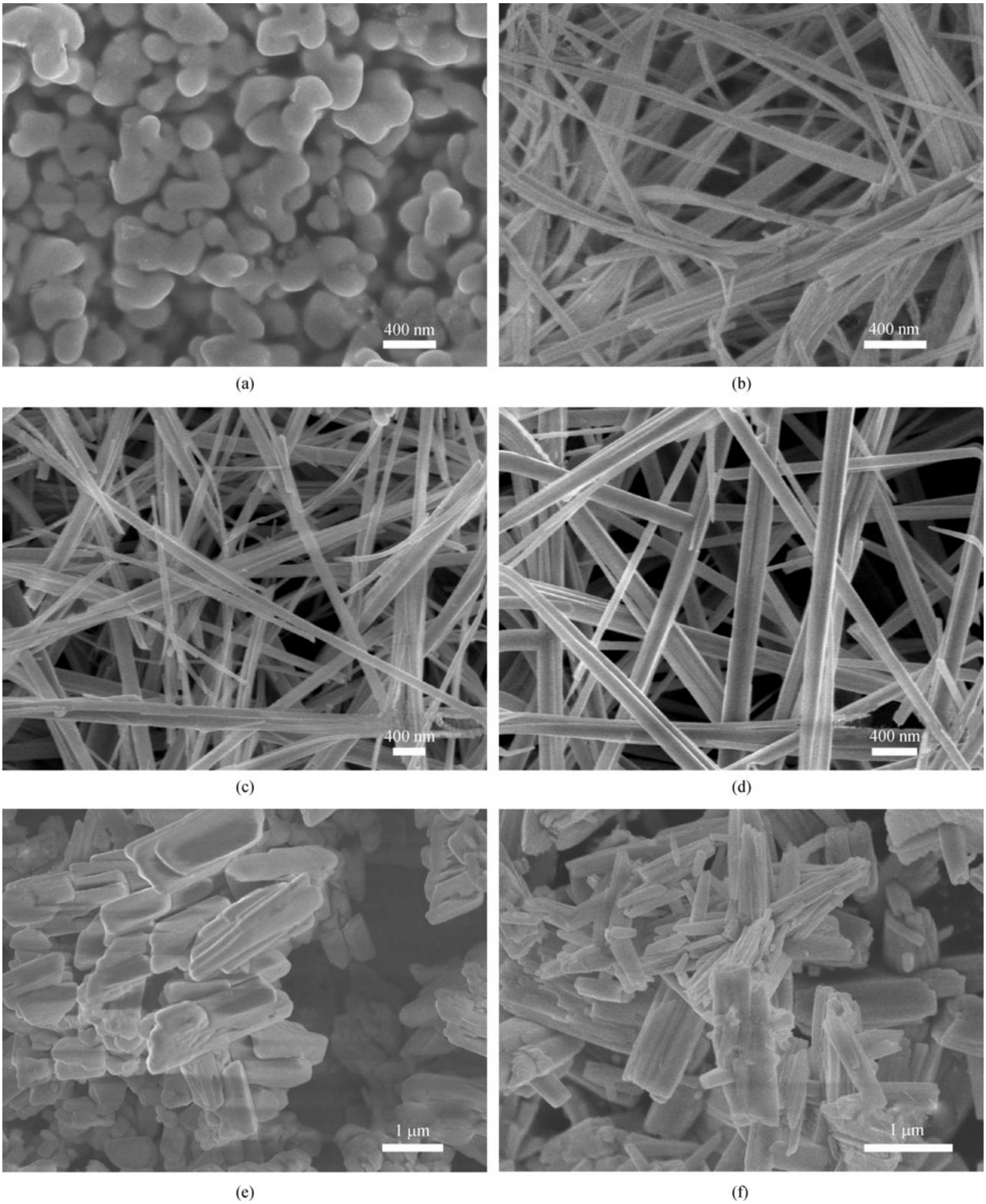
It is known that the crystal structure of t-Se is highly anisotropic, consisting of helical chains of covalently bound selenium atoms with three atom per turn. These chains are held together to form a hexagonal lattice via a mixture of electronic and Van der Waals forces [7]. Because of this anisotropic structure, t-Se has a strong tendency to grow along the *c*-axis direction into a 1D structure. When the conversion from a-Se to t-Se is carried out in ethanol or acetone, the conversion speed is not very fast, and the t-Se can grow in its own manner and finally grow into nanowires. When the conversion is carried out in pyridine or ethylenediamine, the conversion speed is too fast. As a result, the anisotropic growth along the *c*-axis direction is disturbed, and finally microrods instead of nanowires are obtained. Of the solvents we have tried, acetone is an appropriate medium for obtaining t-Se nanowires with a fast speed.

The conductivity of the t-Se nanowires obtained in acetone was measured in a dark box or under illuminated by using a tungsten lamp (220 V, 25 W). The distance of the device-to-light source was 10 cm. The device for measuring the photoelectrical properties of t-Se nanowires was similar to that reported by Liu et al. [22]. Two Au electrodes are fabricated at both ends of the outer alumina ceramic tube by screen-printing. The t-Se nanowires were dispersed into an appropriate amount of ethanol under ultrasonication. Then the suspension solution was dropped onto the outer surface of the ceramic tube. After dried in air, a layer of t-Se nanowires film was coated on the surface of the ceramic tube.

Figure 4(a) shows the *I-V* curves of the t-Se nanowires film measured in the dark and under illumination. The approximately linear shape of the curves reveals a good ohmic contact of the t-Se nanowires with the Au electrodes. It is observed that the current of the t-Se nanowires under illumination gets increased and enhanced by ca. 1.3 times. For the sake of comparison, the photoconductivity of a-Se nanoparticles was also measured. Figure 4(b) shows the *I-V* curves of the a-Se nanoparticles film measured in the dark and under illumination. The current of the a-Se nanoparticles under illumination also gets increased. However, the increase is not as obvious as that of the t-Se nanowires. In addition, t-Se is more stable than a-Se. So t-Se nanowires are a better candidate for the fabrication of photoelectrical nanodevices.

4 Conclusion

In summary, we report on a simple and convenient



(a) (b) (c) (d) (e) (f)

Fig. 3 SEM images. (a) a-Se sample; (b) t-Se nanowires obtained in acetonitrile; (c) t-Se nanowires obtained in ethanol; (d) t-Se nanowires obtained in acetone; (e) t-Se microrods obtained in pyridine; (f) t-Se microrods obtained in ethylenediamine

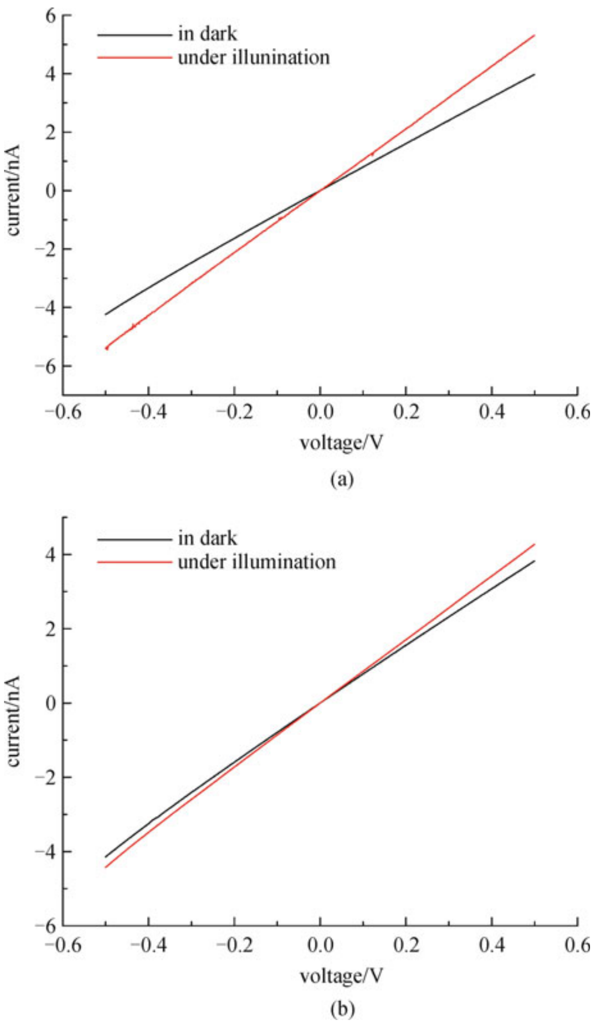


Fig. 4 (a) *I-V* curves of the t-Se nanowires film measured in a dark box and under illumination by using a tungsten lamp (220 V, 25 W); (b) *I-V* curves of the a-Se nanopartilces film measured in a dark box and under illumination

method to prepare t-Se nanowires with uniform sizes. The t-Se nanowires were obtained through the conversion from freshly prepared a-Se nanoparticles in acetone at room temperature. The experimental results show that acetone can dramatically promote the conversion from a-Se to t-Se, and the inherent anisotropic growth habit of t-Se leads to the formation of t-Se nanowires. The photoelectrical properties of t-Se nanowires and a-Se nanoparticles were investigated, and the results show that the t-Se nanowires have better photoelectrical properties than that of the a-Se nanoparticles. The t-Se nanowires may find wider application in fabricating photoelectrical nanodevices.

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