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The effect of KI on the formation of Tl_2E (E = S, Se) nanorods via solvothermal route

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Abstract

Tl_2E (E = S or Se) nanorods were synthesized via solvothermal route with the addition of KI. The products were characterized with X-ray powder diffraction patterns and transmission electron microscope images. Their optical properties were studied by UV–vis transmittance and photoluminescence spectrum. The band gap of direct forbidden transitions was found larger than that of bulk materials, because of the blue shift caused by nanometer-scale crystalline particles due to quantum confinement effects. A possible growth mechanism is proposed.

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Keywords: A. Nanostructures; B. Crystal growth

1. Introduction

In recent years, one-dimensional (1D) nanostructural materials have become an exciting research focus because of their great potential of addressing some basic issues about dimensionality and space-confined transport phenomena [1]. However, the fabrication or synthesis of these 1D nanostructural materials is a challenge owing to their extremely small size and their large anisotropy. Nowadays, much attention has been paid to Tl_2E (E = S or Se) because of their various interesting and potentially useful electrical properties. These studies mainly stemmed from the detection of photoconductivity and photovoltaic effect in Tl_2S and semiconduction of Tl_2Se [2,3]. Traditionally Tl_2S was synthesized using thallium ethoxide in ethanol and dry H_2S [4,5], while the compound of Tl_2Se was prepared [4] by heating the component elements in a sealed tube at about 400 °C.

Recently, the chemical solution routes are emerging as effective, convenient and less energy-consuming synthesis methods [6–8]. Because solvothermal route is one of the most promising preparations [9], we employed it to prepare thallium(I) sulfide and thallium(I) selenium nanorods.

2. Experimental procedure

All reagents were of analytical grade purity and were purchased from Shanghai Chemical Co. Ltd. The typical procedure for the preparations is as follows: 0.01 mol of Tl_2SO_4, 0.01 mol sulfide powder and 0.005 mol KI were added to a Teflon reactor of 50 ml capacity, then ethylenediamine was filled into 90% of the total volume. The reactor was maintained at the temperature of 150 °C for 48 h. Then the products were collected, washed with ethanol and dried in vacuum at 60 °C for 6 h.

The phase and the crystallographic of the products were characterized by X-ray diffraction (XRD) pattern, which was recorded by using a Shimadzu XRD-6000 X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm), the scanning rate of 0.05° s^{-1} was applied to record the pattern in the 2θ range of 10–70°.

The transmission electron microscope (TEM) image was

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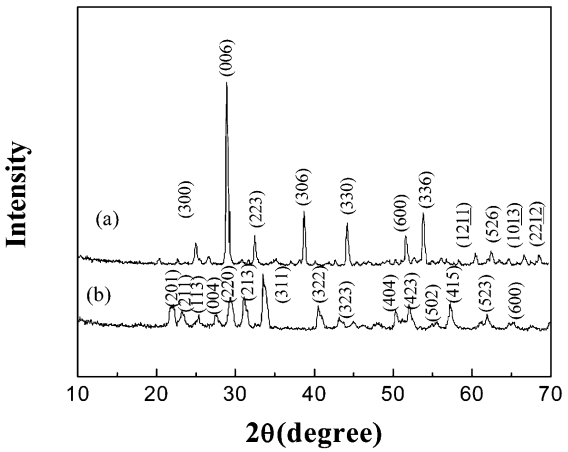


Fig. 1. (a) The XRD pattern of as-prepared products, which indicates a hexagonal phase of Tl_2S. (b) The XRD pattern of as-prepared products, which indicates a tetragonal phase of Tl_2Se.

taken with a Hitachi Model H-600 TEM, using an accelerating voltage of 75 kV to determine the morphological features. Samples were prepared by placing a drop of dilute alcohol supersonic disperser, onto a carbon-coated copper grip and allowing the alcohol to evaporate in the dark.

UV–vis absorption spectra were measured on a Hitachi U-4100 spectrophotometer with the samples dispersed in alcohol at room temperature model. Photoluminescence (PL) spectra were recorded using a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

3. Results and discussions

The XRD pattern of as-prepared products (Fig. 1(a)), showed the presence of reflections characteristic of the Tl_2S hexagonal phase of the products. The intense peaks indicate that the as-prepared products have high degree of crystallinity. The lattice constants calculated for the sample are $a = 1.221 \pm 0.008$ nm; $c = 1.829 \pm 0.01$ nm, which is in agreement with the values of $a = 1.222$ nm, $c = 1.821$ nm reported by JCPDS 06-378.

The typical morphology of Tl_2S products is presented in Fig. 2(a) via TEM observations. They all take the shape of nanorods with the average size of 100 nm in diameter and length up to 1.7 μm.

The optical property of the products was also investigated. Fig. 3(a) shows the transmittance spectrum of Tl_2S

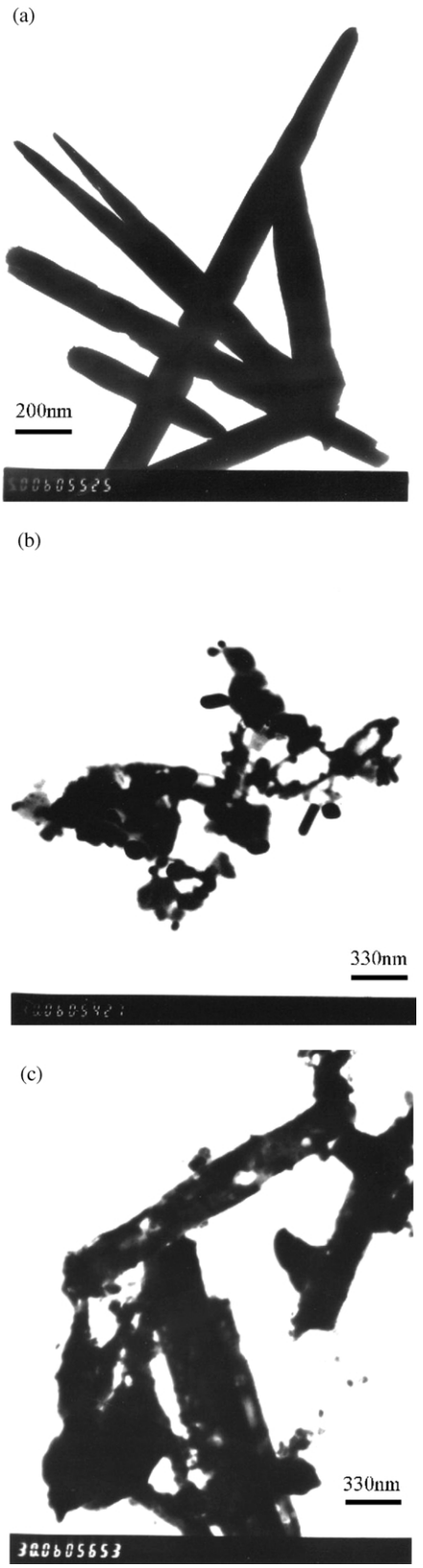
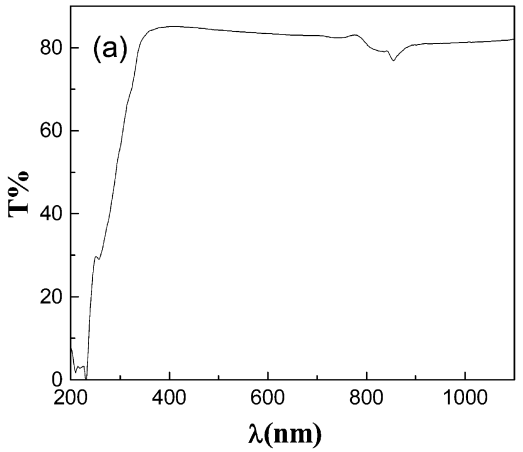


Fig. 2. (a) TEM image of many Tl_2S nanorods with the addition of KI. (b) TEM image of Tl_2S nanorods without the use of KI. (c) TEM image of many Tl_2Se nanorods with the addition of KI.



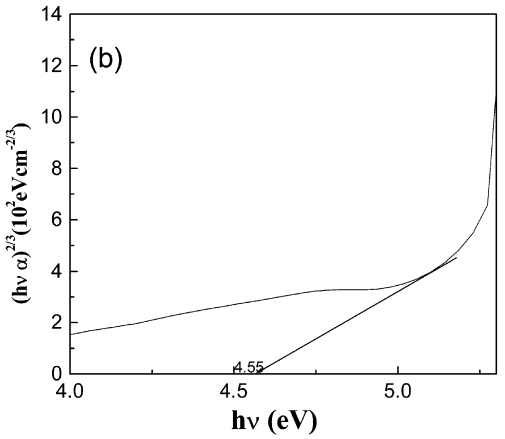


Fig. 3. (a) The transmittance spectrum of Tl_2S. (b) The $(h\nu\alpha)^{2/3}$ versus photon energy ($h\nu$) of Tl_2S.

products. The clear maximum at 370 nm is assigned to the optical transition of the first excitonic state.

According to Smith [10], the value of $(h\nu\alpha)$ in semiconductors is proportional to $(h\nu - Eg)^n$, where h is Planck's constant and ν, the frequency of the optical radiation absorbed. Hence a plot $(h\nu\alpha)$ versus $(h\nu)$ would yield straight-line plots, with Eg as the intercept on the $(h\nu)$-axis. The optical transitions and hence the band gap are classified as direct, direct forbidden, indirect, and indirect forbidden for $n = 1/2, 3/2, 2$ and 3, respectively. The band gap of Tl_2S is classified as direct forbidden and the value of n is equal to 2/3 [11]. So we plot $(h\nu\alpha)^{2/3}$ versus $(h\nu)$, shown in Fig. 3(b) and obtain the value of the band gap 4.55 eV. The value is larger than that of bulk materials [11], which would be the blue shift caused by nanometer-scale crystalline particles due to quantum confinement effects.

PL emission spectrum of Tl_2S is shown in Fig. 4. The emission spectrum was measured with 280 nm excitation source. The maximum is at 370 nm.

The possible growth mechanism is proposed. We

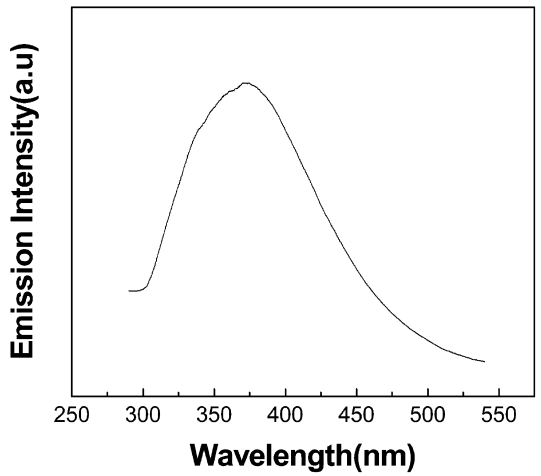


Fig. 4. PL spectrum of as-prepared Tl_2S nanorods.

speculate that the presentation of KI plays an important role. During the formation of nanorods, Tl_2S nucleus absorb anion (I^-) on crystal planes selectively and grow large along the c-axis direction, which makes the nanoparticles long and slim. To confirm our proposed mechanism, we did control experiment without the addition of KI, keeping the other experimental variables invariant, the nanoparticles could develop in rod-like shape but irregular, as shown in Fig. 2(b).

The synthesis route may be used to other systems. When selenium powder was used as starting material instead of sulfide powder, Tl_2Se was obtained.

The XRD pattern of Tl_2Se products shows strong peaks and can be indexed to tetragonal phase, as shown in Fig. 1(b). The lattice constants calculated for the sample are $a = 0.855 \pm 0 : 001$ nm; $c = 1.267 \pm 0.003$ nm, which is good according to the values of $a = 0.854$ nm, $c = 1.270$ nm reported by JCDPS 47-1299.

Fig. 2(c) is the TEM image of Tl_2Se, which show inhomogeneous nanorods. The size of Tl_2Se nanorods is about 75 nm in diameter and 900 nm in length, which is smaller and shorter than that of Tl_2S. The morphology of Tl_2Se is not good because it is sensitive to electron beam irradiation during the examination, which is expected due to its low melting point (340 °C) while Tl_2S melts at 448 °C. We also did control experiment without the addition of KI, the nanopaticles could develop in rod-like shape, too.

The transmittance spectrum of Tl_2Se was also measured. Like Tl_2S, we plotted $(h\nu\alpha)^{2/3}$ versus $(h\nu)$ and got the value of the band gap 3.10 eV. The maximum in the PL emission spectrum of Tl_2Se is at 379 nm when 250 nm excitation source was used.

4. Conclusion

Under the solvothermal route, nanorods Tl_2E (E = S, Se) were synthesized, with the additional KI, approving

morphology was obtained. The solvothermal route is easy to be maintained and controlled. This method may be useful in the synthesis of the other composite materials.

Acknowledgements

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