

ZnO nanorods grown on ZnSe particles by the Chemical Vapor Deposition Method

Chongfeng Guo¹, Wallace C. H. Choy^{1*}, Y.B. Leung¹, K.W. Cheah², Yueping Fang³

¹ Department of Electrical and Electronic Engineering, the University of Hong Kong, Pokfulam Road, Hong Kong, China.

² Department of Physics, Hong Kong Baptist University, Kowloon, Hong Kong, China.

³ School of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin, Guangxi, 541004, P.R. China.

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* Author to whom correspondence should be addressed

W.C. H. Choy

Department of Electrical and Electronic Engineering

The University of Hong Kong,

Hong Kong SAR, P. R. China

Tel and Fax:

Electronic mail: chchoy@eee.hku.hk

Abstract:

A novel structure of ZnO nanorods on microsized ZnSe particles has been prepared through a chemical vapor deposition (CVD) technique using Zn and Se powders as the sources. The dimension of the nanorods can be controlled by adjusting the growth temperature, time and the Zn:Se ratio. Through the investigation of the effects of synthesis time and Zn:Se ratio on the formation of ZnO nanorods on ZnSe micro-particles, it is proposed that the synthesis of the ZnO-ZnSe structures involves a two-stage formation. The growth of ZnO nanorods can be described by VS mechanism. The photoluminescence (PL) of the ZnO-ZnSe structures has also been studied.

Introduction

The direct wide band-gap semiconductors such as most of the Zn and Cd based II-VI compound semiconductors are of the great interest for use in blue and ultraviolet (UV) optical devices [1,2]. Zn-based II-VI compound semiconductors have already been utilized in a wide range of applications. For instance, ZnO has been used for solar cell windows, transparent conductive films, catalysis, gas sensors and short-wave optics [3,4]. ZnSe has been applied for use in saturable-absorber Q switch, blue-green laser diode, modulated waveguide and blue-ultraviolet photodetector [5]. Meanwhile, intense efforts have been put into studying quasi-one-dimensional II-VI compound semiconductors during the past decades because of their unique quantum properties and their potential for nanoscale electronic and optoelectronic integrated devices. Many active researches have been focused on the synthesis of 1-D II-VI compound semiconductors through different methods, such as solvothermal route[6], laser-assisted catalytic growth[7], surfactant-assisted chemistry method [8,9], metalorganic chemical vapor deposition (MOCVD) [10] and chemical vapor deposition (CVD) method [11]. Among these methods, CVD method is the most popular one.

Here we present a novel structure of ZnO nanorods grown on the surface of micrometer-sized ZnSe particles. The synthesis is based on chemical vapor deposition (CVD) of Zn and Se powders under controlled conditions without the use of catalyst. The effects of the residual oxygen in the reactor on the synthesis of nanorods will be investigated through changing the usage of the Se powder and adding the carbon powder in the sources. We also study the effects of the growth time and temperature. The chemical composition, structural and optical properties of the sample were also investigated using

scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and photoluminescence (PL).

Experimental procedures

ZnO nanorods grown on the surface of ZnSe grain particles were prepared by thermal evaporating Zn and Se powders in N₂ filled chamber without the presence of catalyst. The furnace setup used in this study is illustrated in Fig. 1. A quartz tube was set horizontally inside the furnace. Zinc and selenium powders in two separate alumina crucibles were placed at different temperature zones inside the quartz-tube chamber. The crucible with selenium was placed nearer to the gas input at a lower temperature zone while zinc source was placed at the central region of the furnace of a higher temperature zone. An Al₂O₃ substrate was also placed at the downstream of the quartz tube at about 2.5cm away from the crucible filled with Zn powder. Then the tube was pumped down to a pressure of about 10⁻² Torr. The total pressure was maintained at 300 Torr during the whole fabrication process when N₂ gas was introduced into the quartz tube at a constant flow rate of 150 sccm (standard cubic centimeter per minute). After the growth process, the furnace was gradually cooled down to room temperature by turning off the power supply. A layer of yellow colored sample was formed on the inner-wall of the crucible of zinc powder.

The sample scrapped from the inner-wall was characterized and analyzed by scanning electron microscopy (SEM, Jeol JEM 2000FX), high-resolution transmission electron microscopy (HRTEM, Philips Tecnai 20), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD, Rigakau, D/Max with Cu K α radiation). The specimens for TEM

were prepared by mixing the synthesized products in ethanol and dispersing them in an ultrasonic bath for 20 min. The resulting mixtures were dropped onto a TEM grid for measurement. Photoluminescence (PL) at the 20K was performed in a cryostat. The excitation source is He-Cd laser with a wavelength of 325nm. During the measurement, the power of the laser beam at the sample holder was kept at about 0.4mW.

Results and discussion

The X-ray diffraction (XRD) pattern of the yellow products prepared at 650°C and the ratio of Zn: Se=1:1 in weight is shown in Fig.2. A set of diffraction peaks with strong intensity can be indexed as those from the known zinc-blende structure of ZnSe, with a lattice constant of $a=0.5675\text{nm}$. This matches very well to the data in the literature within a small experimental error (JCPDS, file No.:37-1463; $a=0.5668\text{nm}$; error is 0.12%). The results indicate that the main component of the products is zinc-blende cubic ZnSe while the details of the chemical composition of synthesized materials will be further investigated by HRTEM, EDS and SAED.

The as-synthesized samples are first analyzed by scanning electron microscopy (SEM) to determine the relationship between the growth temperature and their morphologies. Fig.3 (a), (b), (c) and (d) show the typical FESEM images of as-prepared samples grown at different temperatures 550°C, 600°C, 650°C and 700°C, respectively. Particles with different diameters (up to micrometer) and irregular shapes are observed, and the nanorods randomly grow on the surface of the particles. It is interesting to note that the morphology shows a wool-ball-like structure in Fig.3 (b) and (c). The majority of the wool-ball-like structures are composed of two parts, micron-sized particles and nanorods

or nanowires which are grown around the surface of the particles. Diameter of the nanorods mainly ranges from 15 to 100nm and their length extends from 100nm to 1 μ m. The nanorods generally exhibit a hexagonal cross-section as displayed in the inset of Fig.3(c). The amount of nanorods can be controlled by tuning the growth temperature. As shown in Fig.3, a large amount of nanorods are obtained at the temperature range of 600-650°C.

The influence of the growth time on the nanostructures has also been investigated using the synthesis time of 15, 30, 60 and 120 min at the temperature of 650°C when the other growth parameters are kept constant. The SEM images of Fig. 4 and Fig.3(c) illustrate the formation of the nanostructures as a function of the growth time. Nanometer-sized seeds are first grown on the surfaces of ZnSe particles as shown in Fig.4a when the growth time is 15 min. Meanwhile, some facets of the particles are still smooth and clean. This implies that nanosized seeds begin to grow on the surface of ZnSe particle after the formation of ZnSe particle. By increasing the synthesis time to 30min, nanorods are obtained as shown in Fig.4b. The lengths of the nanorods extend to about 1 μ m when the growth time is increased to 60 min as shown in Fig.3c. When the growth time is further increased to 120 min (see Fig.4c), the nanorods on the surface of the particle become longer and some scattered nanowires are obtained as shown in the inset of Fig. 4c. Their diameter and length can be up to about 150nm and several micrometers, respectively. As a consequence, it is believed that the formation of the novel structure can be described by a two-stage process. The first stage is the growth of the particle and the second stage is the nucleation and growth of the nanorods on the surfaces of the micro-particles. When

the growth time is short, seeds are found on the particles. With the increase of the growth time, the nanorods are formed. The length and diameter of the nanorods increase with the growth time. The formation mechanism of the nanorods on particles will be discussed in detail later.

As shown in Fig. 5(a) and (b), the EDS results reveal that the products contain nanosized ZnO rods and microsized ZnSe particles. Fig. 5(d) shows a TEM image of nanorods on the surface of a microparticle, revealing the representative morphology of the sample. The average diameter of the ZnO nanorods is around 20 nm. The HRTEM image shown in Fig.5(c) shows the atomic structure of a single nanorod. The continuous lattice fringes indicate that the ZnO nanorod is of a single crystal. Its growth direction is along [0001] and the spacing between two fringes is 0.52nm. The Fourier transform of the HRTEM image is given in the inset of Fig. 5(c).

In the experiment, Zn and Se powders are used as the source materials and pure nitrogen is used as the carrier gas. The oxygen for the formation of ZnO nanorods is from the source powders, residual oxygen and moisture in the furnace setup [12-14]. To study the effect of oxygen in the growth of ZnO nanorods, a series of experiments are conducted by adjusting the weight ratio of Zn:Se from 2:1 to 1:5 while keeping the other parameters the same. The growth time and temperature are 60 min and 650°C respectively. Fig. 6(a) to (c) are the FESEM images of the as-synthesized sample with weight ratios of Zn/Se corresponding to the 2:1, 1:1 and 1:5, respectively. With the decrease of Zn:Se ratio by increasing the weight of Se source and maintaining the weight of Zn constant, the length

of ZnO nanorods grown on the surface of ZnSe particles becomes shorter and shorter. When the Zn:Se ratio = 2:1, the lengths of the nanorods can be over 1 micrometer as shown in Fig.6(a). The length of the nanorods reduces in the case of 1:1 ratio (see Fig.6b) and becomes seeds with only a few nanometer long on the surface of the ZnSe particles when Zn:Se ratio is 1:5 as shown in Fig.6(c). It is worth to note that some Se powder remains in the crucible for the case of 1:5 while there is no Se powder left in the crucible after the reaction for the cases of 2:1 and 1:1. The results show that the formation of nanorods depends on the partial pressure of selenium and oxygen. During the initial stage of the synthesis, an abundant of selenium source is present and its partial pressure is high, the conditions favor the formation of ZnSe particles. In the later stage of the synthesis, the partial pressure of selenium reduces, especially when the Se source is almost completely evaporated. The partial pressure of oxygen becomes significant and ZnO nanorods are formed. The results further support the two-stage formation theory of ZnO nanorods on ZnSe microparticles discussed previously. We have also placed some active carbon powder in the reactor to minimize the residual oxygen in the reactor. The result, as expected, is that no ZnO nanorod is formed on the surface of the ZnSe particle as shown in Fig.6(d).

From the effects of synthesis time and Zn:Se weight ratio as discussed previously, we postulate that the growth of the novel ZnO-ZnSe structure can be described by a two-stage process. The first stage is the growth of ZnSe particle. At the synthesis temperature of 550°C to 700°C, vapor phase Zn and Se atoms encounter each other, they undergo a condensation reaction leading to the formation of single-crystalline nuclei of

ZnSe. The ZnSe nuclei have a high surface energy and continuously undergo surface growth reaction by interacting with gaseous precursors. The ZnSe particles coagulate together on the inner and outer walls of the Zn filled crucible, the Al₂O₃ downstream substrate and the surface of the quartz tube. The growth of ZnSe particles will diminish when the selenium source is almost completely evaporated and the selenium partial pressure decreases to a certain level.

It should be noted that by comparing Fig.7(a) and Fig.7(b), we also find that the average size of ZnSe particle collected from inner-wall was larger than that from the outer-wall of the crucible or from the Al₂O₃ substrate in the downstream of the reactor, which is in good agreement with the result of E. M Gavrushchuk [15] that fine-grained powders are obtained in the reagents with a lower vapor composition.

The second stage is the growth of the nanorods. The metal-catalytic vapor-liquid-solid (VLS) process is one of the mechanisms to account for the growth of 1-D nanorods or nanowires. For metal-catalytic VLS, the growth mechanism typically involves a liquid metal catalytic particle located at the tip of the nanowires [16,17]. In our experiment, no metal catalyst is used and no alloy particle is observed at the tips of the nanorods. Therefore, the metal-catalytic VLS mechanism can be ruled out as the growth mechanism in our work. Our results show that ZnO nanorods on the ZnSe particles (see Fig.7a) can only be collected from the inner-wall of the crucible filled with Zn where the partial pressure of Zn is very high. The ZnSe particles collected from the outer-wall of the crucible, the alumina substrate in the downstream of the reactor (inset of Fig.7b) and the

wall of quartz tube do not have ZnO nanorod. Therefore, we can conclude that high Zn partial pressure plays an important role in the formation of ZnO nanorods. The high local Zn partial pressure in the Zn powder filled crucible leads to super-saturation and the formation of liquid droplets of Zn on the surface of ZnSe particles. When the gaseous Se atoms diminish due to the complete evaporation of the Se source, the Zn vapor reacts with the gas-phase oxygen from the chamber to generate ZnO nanostructures. Consequently, the synthesis of the ZnO nanorods can be considered as a VS process [18].

Figure 8 illustrates the photoluminescence (PL) spectra of the as-prepared sample with the Zn/Se ratio of 1:5, 1:2 and 1:1, at 20K. There are three emission bands present in the PL spectra of the samples with 1:1 and 1:2 Zn/Se ratios (Fig.8c and b), including a strong orange emission at around 600nm and a small blue peak at about 462nm as well as a weak but resolvable blue-green peak at around 500nm. The emission at around 462nm is usually attributed to the donor-acceptor pair transition of ZnSe [19]. The strong orange emission at about 600nm is associated with the vacancies of Zn in ZnSe. This emission band is often observed in bulk ZnSe, which is interpreted as a well known 'self-activated' luminescence in II-VI compounds due to the recombination of shallow donor-deep acceptor pairs [20]. As the other weak blue-green emission at around 500nm, it has been reported in [21] and may be due to the effects of the residual pressure of H₂O and O₂. However, we cannot find the near band edge UV emission at around 375nm of the free excitonic emission of ZnO nanorods which is usually very sharp and strong [22]. The possible reason is that the emission at around 375nm is absorbed by the ZnSe particle because the absorption region of ZnSe ranges from 325nm to 425nm [23]. On the other

hand, the relative peak intensity of emission at 600nm (I_{600}) becomes weaker comparing with that of 462nm (I_{462}) when the Zn:Se ratio is changed from 1:1 to 1:9. The ratio of I_{600}/I_{462} is about 10:1, 3:1 and 1:9 when the Zn:Se ratio increases from 1:1 to 1:2 and then 1:9, respectively, which indicates that the density of defects in ZnSe particle becomes smaller with the increasing Se usage in the experiment.

Conclusion

In conclusion, we have fabricated single-crystal ZnO nanorods on the surface of microsized ZnSe particles by CVD method using Zn and Se as the sources. The SEMs images show that the formation of ZnO nanorods can be controlled by synthesis time, temperature and amount of the sources. HRTEM reveals that the nanorods grow along the [0001] direction and are single crystals. Since the ZnO nanorods on ZnSe particles can only be collected from the inner-wall of the crucible filled with Zn source at which the partial pressure of Zn is high, the partial pressure of Zn plays an important role in the formation of the ZnO nanorods. The growth of the ZnO nanorods can be described as a VS mechanism. Through the investigation of the effects of growth temperature and the weight ratio of Zn:Se on the formation of the novel ZnO-ZnSe structures, we postulate that the synthesis process involves two stages which are (1) the formation of ZnSe micro-particles followed by (2) the formation of ZnO nanorods on ZnSe particles. PL spectra of samples with different ratios of Zn:Se at 20K have been investigated. The defects in ZnSe particles reduce with the increasing Se usage in the experiment.

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Captions

- Fig.1 Schematic diagram of the experimental apparatus used in the growth of ZnO-ZnSe structures.
- Fig.2 XRD pattern of the sample prepared at 650°C for 60mins. The ratio of Zn:Se is about 1:1.
- Fig.3 FE-SEM images of ZnO nanorods or nanowires grown on the surface of ZnSe particles at various temperatures (a) 550°C, (b) 600°C, (c) 650°C, and (d) 700°C for 60mins with the Zn:Se ratio of 1:1.
- Fig.4 FE-SEM of sample prepared at 650°C with different growth time: (a) 15mins, (b) 30mins, (c) 120mins. The ratio of Zn:Se is 1:1.
- Fig.5 (a) EDS of nanorods, corresponding to circle A in figure (d), (b) EDS of particle, corresponding to circle B in figure (d), (c) HRTEM image of nanorods with the growth direction of [0001]. The inset is the corresponding Fourier transform, (d) The TEM image of the sample prepared at 650°C for 60mins. The ratio of Zn:Se is about 1:1.
- Fig.6 FE-SEM image of sample prepared at 650°C for 60mins with different Zn:Se ratio: (a) 2:1, (b) 1:1, (c) 1:5, (d) mixing carbon with Zn. The other parameters are kept constant.
- Fig.7 FE-SEM image of sample collected from the inner-wall of crucible and the Al₂O₃ substrate in the downstream of the Zn crucible. The sample is prepared at 650°C for 60mins and the ratio of Zn:Se is 1:1.
- Fig.8 PL of the sample prepared at 650°C for 60min with different Zn:Se ratios at 20K temperature: (a) 1:5, (b) 1:2, (c):1:1.

Fig.1 Schematic diagram of the experimental apparatus used in this work.

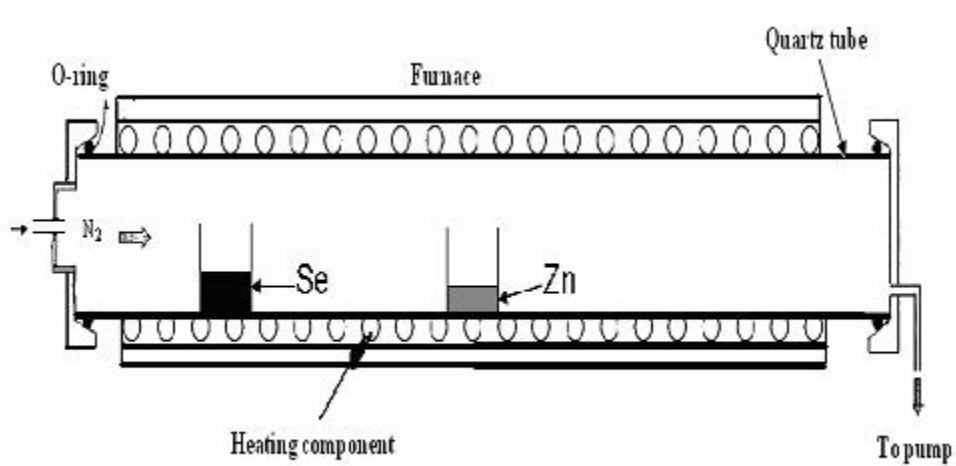


Fig.2 XRD pattern of the sample prepared at 650°C for 60mins. The ratio of Zn:Se is about 1:1.

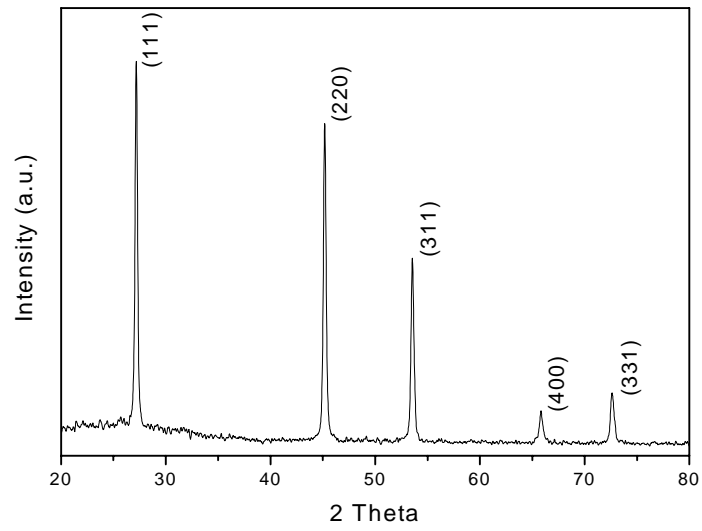


Fig.3 FE-SEM images ZnO nanorods or nanowires grown on the surface of ZnSe particles at various temperatures (a) 550°C, (b) 600°C, (c) 650°C, and (d) 700°C for 60mins with the ratio of Zn:Se as 1:1.

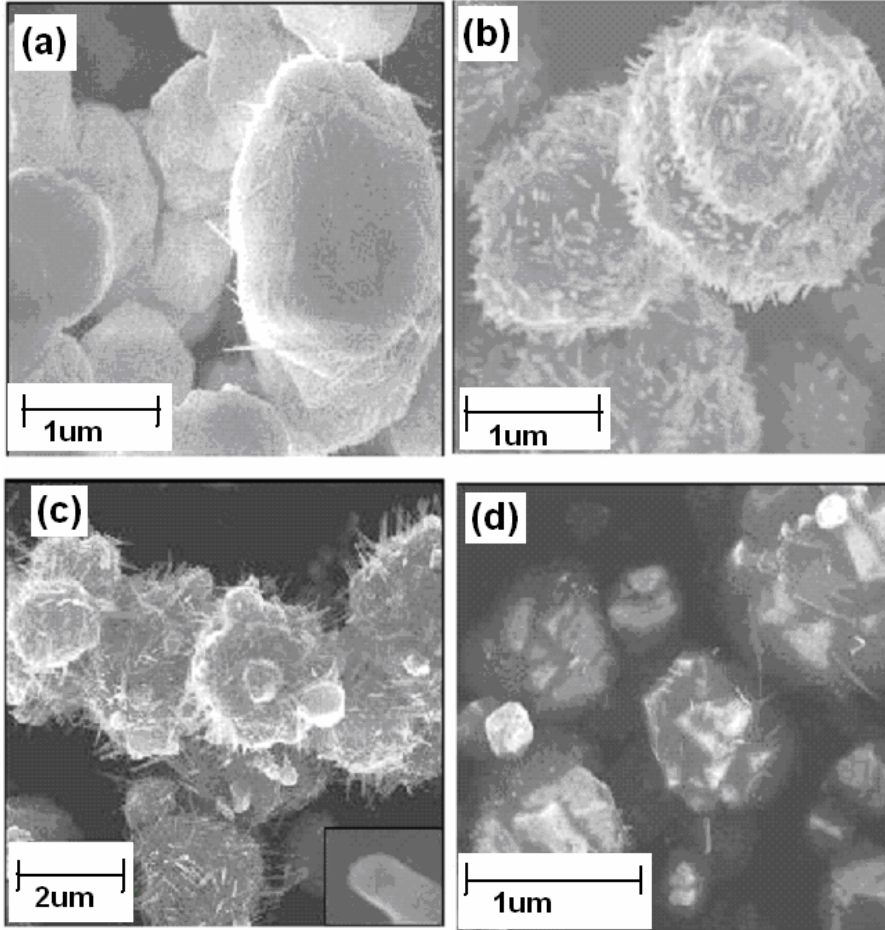


Fig.4 FE-SEM of sample prepared at 650°C with different growth time: (a) 15mins, (b) 30mins, (c) 120mins. The ratio of Zn:Se is 1:1.

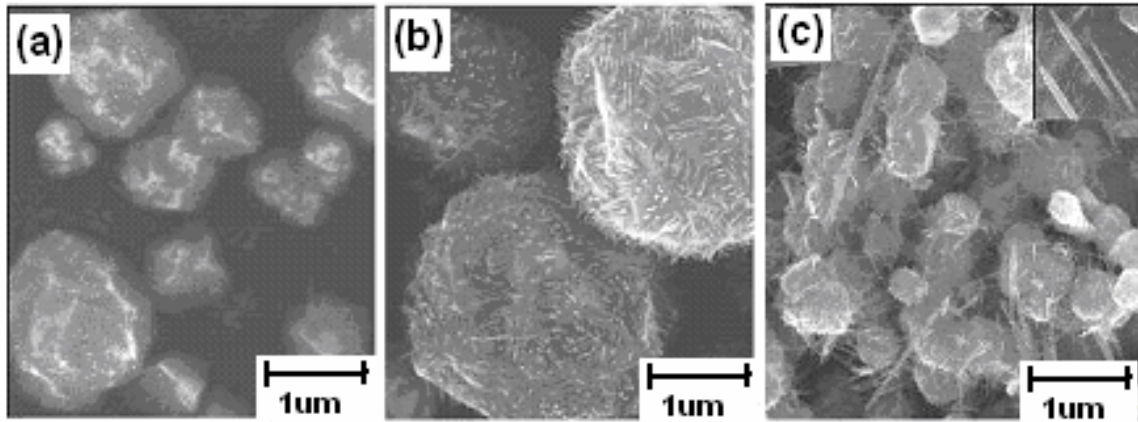


Fig.5 (a) EDS of nanorods, corresponding to circle A in figure (d), (b) EDS of particle, corresponding to circle B in figure (d), (c) HRTEM image of nanorods with the growth direction of [0001]. The inset is the corresponding Fourier transform, (d) The TEM image of the sample prepared at 650°C for 60mins. The ratio of Zn:Se is about 1:1.

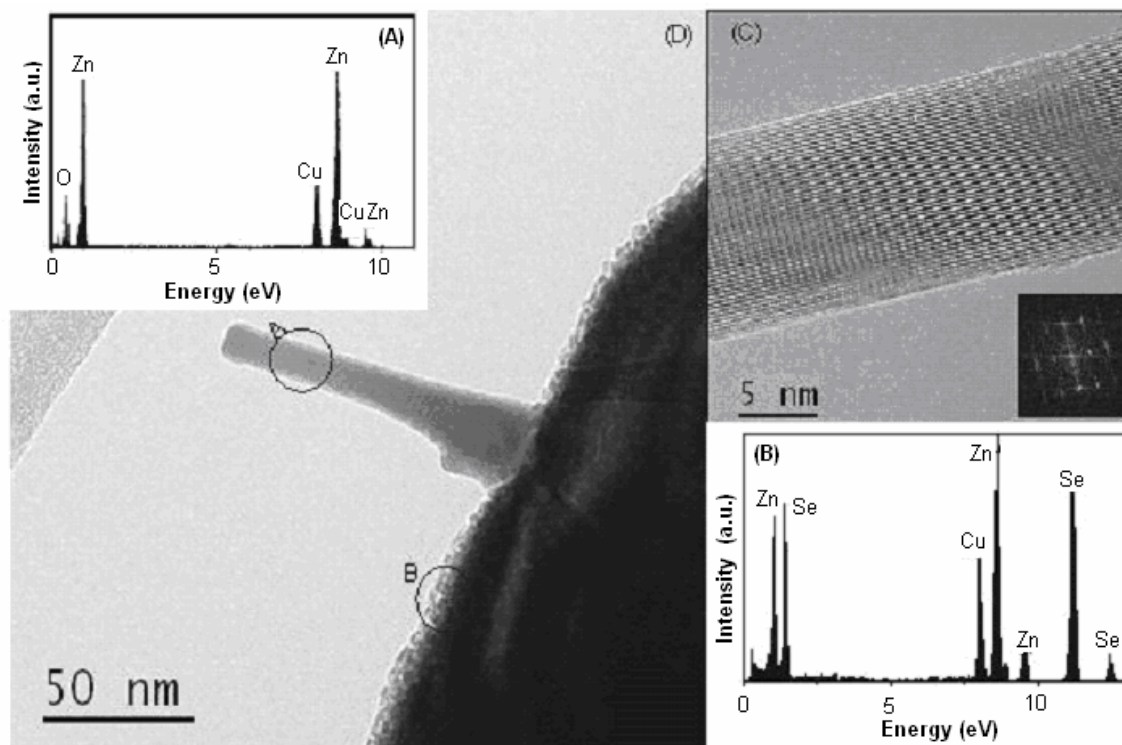


Fig.6 FE-SEM image of sample prepared at 650°C for 60mins with different Zn:Se ratio:

(a) 2:1, (b) 1:1, (c) 1:5, (d) mixing carbon with Zn. The other parameters are kept constant.

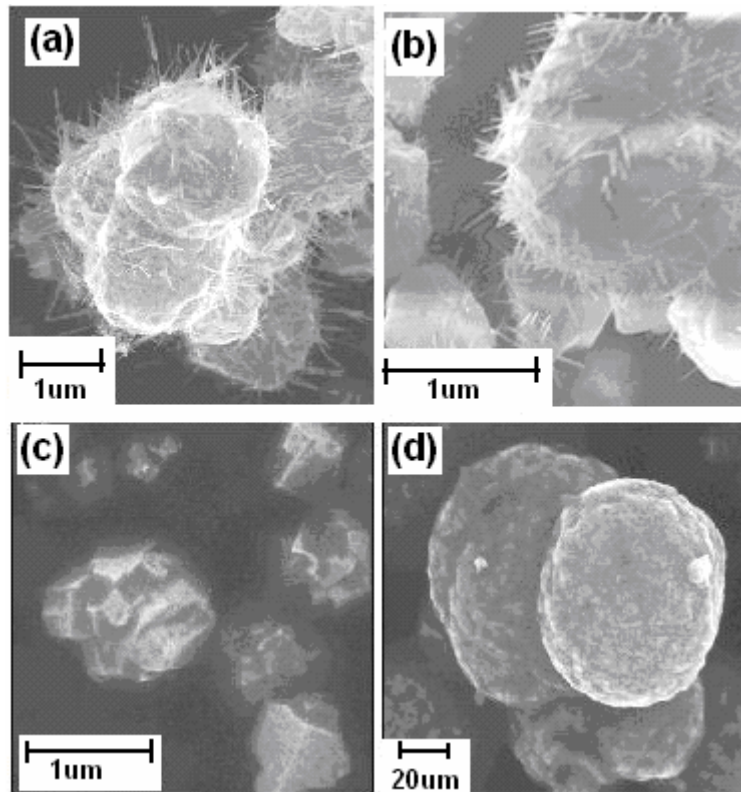


Fig.7 FE-SEM image of sample collected from the inner-wall of crucible and the Al_2O_3 substrate in the downstream of the Zn crucible. The sample is prepared at 650°C for 60mins and the ratio of Zn:Se is 1:1.

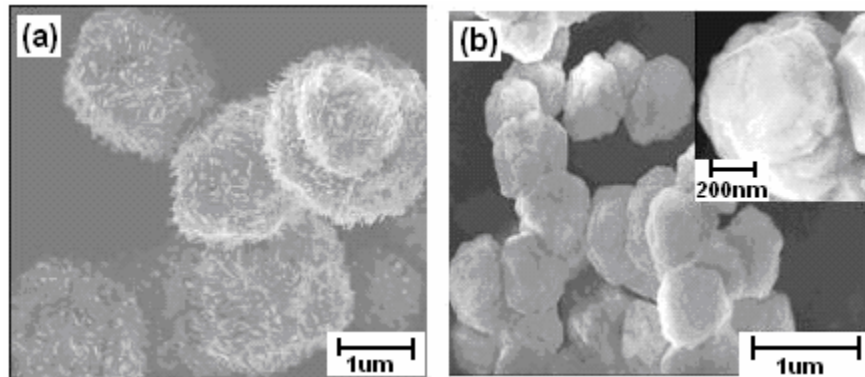


Fig.8 PL at 20K of the sample prepared at 650°C for 60min with different Zn:Se ratios at 20K temperature: (a) 1:5, (b) 1:2 , (c):1:1.

