

## SYNTHESIS OF ZnSe NANOCRYSTALS FOR SOLID-STATE LIGHTING APPLICATIONS

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**Abstract.** We report the large-scale synthesis of highly luminescent ZnSe nanocrystals (NCs) by a simple and low-cost hydrothermal method. XRD (X-ray Diffraction) and HR-TEM (High Resolution Transmission Microscopy) characterization studies confirmed the formation of as-synthesized ZnSe NCs in cubic structure. The optical property of ZnSe NCs was tunable via controlling the Zn:Se molar precursor ratios (0.5:1–1.5:1), reaction temperature (150–200°C), and reaction time (5–30 h). The ZnSe NCs hydrothermally treated at 190°C for 20 h with the Zn:Se precursor ratio of 1:1 exhibited the highest photoluminescence quantum yield after the 355 nm excitation. The current–voltage (*I*–*V*) characteristics of the ZnSe NCs show its promising application in the solid-state lighting.

Keywords: ZnSe; nanocrystals; hydrothermal; photoluminescence; solid-state lighting.

Classification numbers: 78.67.Bf; 78.55.Et.

### I. INTRODUCTION

In recent years, nanocrystals (NCs) have generated a great deal of attention because of their size-tunable properties thanks to quantum confinement effects [1–8]. The synthesis and characterization of II-VI semiconductor NCs have been the subjects of extensive research due to their outstanding potential in optoelectronic applications such as light-emitting diodes (LEDs),

solar cells, sensors, and optical recording materials [9–18]. Among the II-VI semiconductor NCs, cadmium compounds (CdS, CdSe, CdTe, etc.) were widely studied. These materials have so far been the most studied nanocrystal colloid systems. With the controlled growth of particles with diameter between 1.5 and 12 nm, their size-dependent absorption edge covers the entire visible spectra. However, preparation of such small nanocrystals having edges in the UV-blue still remains a challenging task. In addition, these nanocrystals exhibit relatively low quantum yield and broad emission [19–21]. This limits them in the blue and justifies development of other materials such as ZnSe. ZnSe has been reported as an intrinsic semiconductor with a band gap of ~2.70 eV and exhibits a strong luminescence in the blue region, making it a promising material for use in optoelectronic devices, including blue laser diodes, light-emitting diodes (LEDs), and photodetectors [22–26]. This material has also been proposed as a good candidate for biomedical labelling [11,26], as well as for use in other active regions of advanced optoelectronic devices [22–25,27–29].

ZnSe NCs have been synthesized by different methods, including microwave-irradiation [30], reverse micelle [31], thermal evaporation [32], solvothermal or hydrothermal method [33,34], and molecular beam epitaxy [35]. Among these synthesis techniques, the hydrothermal method has been extensively used for preparation of a wide range of nanostructures due to its advantages of low temperature reaction, simple equipment, and less consumption of energy [36].

In this paper, we report on the synthesis and characterization of hydrothermally synthesized ZnSe NCs. The influences of the synthesis parameters on the structure and optical characteristics of the obtained QDs were systematically investigated. The highest quality ZnSe NCs were achieved when the Zn:Se molar ratio was 1:1 and the reaction occurred at 190°C for 20 hours. Our study shows the perspective for a large-scale, low-cost synthesis of ZnSe NCs for applications in solid-state lighting and photovoltaic devices.

## II. EXPERIMENT

### Chemicals

All the chemical reagents used in our experiments were of analytical grade and used as received without any further purification: Zinc powder and selenium powder were purchased from Sigma-Aldrich while sodium hydroxide and absolute ethanol were purchased from Merck.

### Synthesis of ZnSe NCs

ZnSe NCs were prepared according to our previously reported procedure for ZnSe NCs [37]. Selenium (Se) and zinc (Zn) powders were directly used as the starting materials. The molar ratios of Zn:Se were varied from 0.5:1 to 1.5:1.

Firstly, Zn and Se powders were mixed together in a Teflon autoclave (100 ml volume). Then 70 ml of NaOH was poured into this Teflon (70 % of its total capacity). The suspension solution was sealed immediately in the autoclave and soaked at 190°C for 5 hours to 30 hours. After maintaining at this temperature, the autoclave was cooled down to room temperature. The obtained products were ZnSe colloidal solutions. The washing step was done by slowly adding absolute ethanol, followed by centrifugation at 5500 round/min for 15 mins. The solution was decanted to obtain the precipitate. The samples were finally dried at 80°C for 2 hours. The obtained ZnSe powders were light yellow greenish.

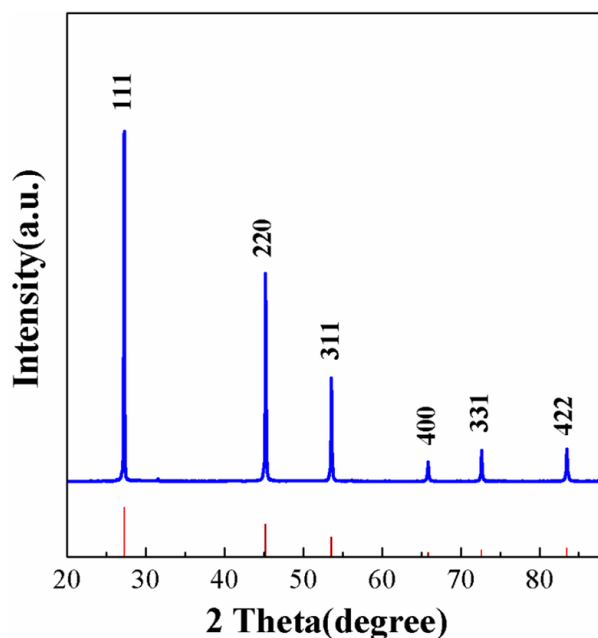
## Characterization

The structures of the obtained samples were investigated by X-ray diffraction (XRD, D8 ADVANCE) and Raman scattering (LabRam HR Evolution with 532-nm laser excitation). Morphology of NCs and their atomic facets could be observed by a high resolution transmission electron microscope (JEM 2100, JEOL). The photoluminescent signal was collected by a 150-grating monochromator (Horiba iHR550) and then detected by a thermoelectrically cooled Si-CCD camera (Synapse) in order to characterize our ZnSe NCs optical properties. The absorption spectra were studied by UV-vis Spectrophotometer (Varian Carry 5000).

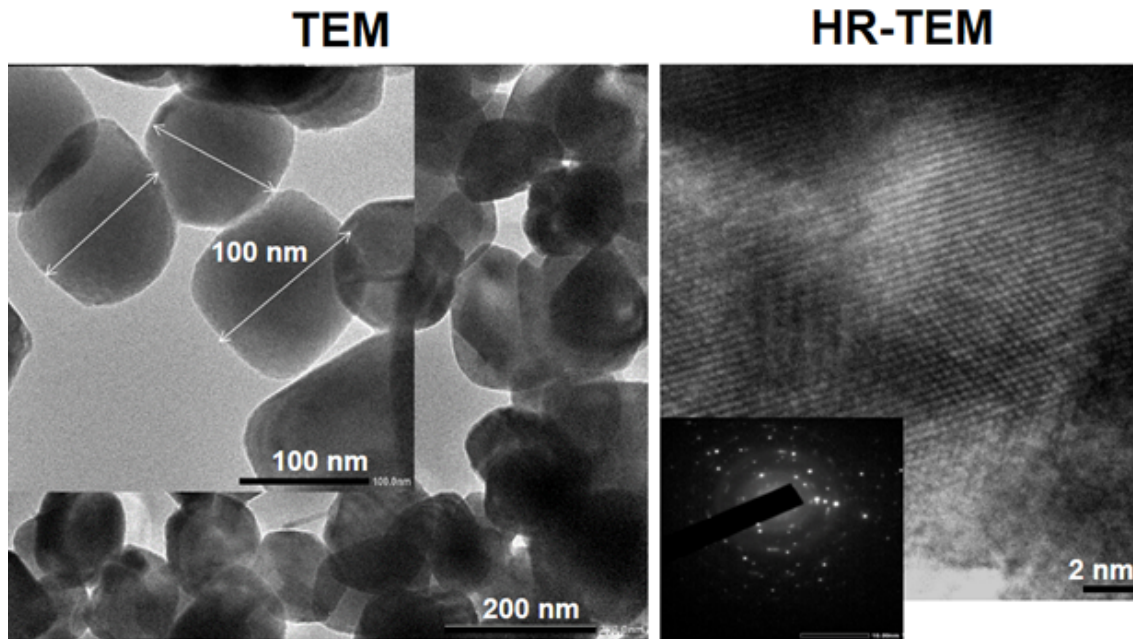
## III. RESULTS AND DISCUSSION

ZnSe NCs were synthesized according to the procedure described elsewhere [37] with some modifications: the Zn:Se molar ratio of 1:1, growth time of 20 hours and the reaction temperature of 190°C. Fig. 1 presents the XRD pattern of the obtained ZnSe powder. The distinct diffraction peaks at the angle  $2\theta$  of 27.22°, 45.19°, 53.56°, 65.83°, 72.62°, and 83.44° could be indexed to (111), (220), (311), (400), (331) and (422) diffraction planes, respectively. All diffraction peaks match well with the standard data for ZnSe (JCPDS/PDF card No. 00-037-1463), indicating that the ZnSe powder is in a cubic phase, similar to those published in the literature for ZnSe NCs [23, 37, 38]. The surface morphology of the as-prepared ZnSe NCs was studied by high-magnified TEM images obtained by the HR-TEM as observed in Fig. 2. The shapes of the ZnSe NCs are varied from sphere to square with the mean size of about 100 nm, which is in good agreement with the value calculated from the XRD pattern using the Scherrer equation [39, 40]. The size of the ZnSe NCs estimated from the Debye–Scherrer formula is about 90 nm (calculated for diffraction peaks at the angle  $2\theta$  of 27.22°).

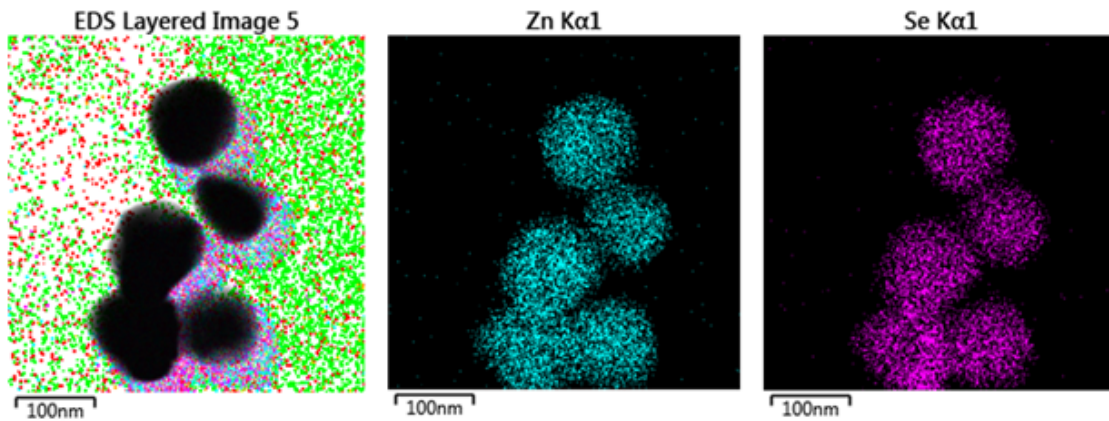
In order to study the structure of the sample in detail, high resolution transmission electron microscope (HR-TEM) measurements were performed. Fig. 2 presents the HR-TEM image of prepared ZnSe NCs and their SAED pattern inset. We calculated the interplanar spacing to be about 0.3 nm, which corresponds to the (111) plane of cubic ZnSe. The HR-TEM image depicts the clear view of lattice planes and the inset shows their diffraction information of sample (the



**Fig. 1.** XRD pattern of ZnSe NCs with the Zn:Se molar ratio of 1:1.



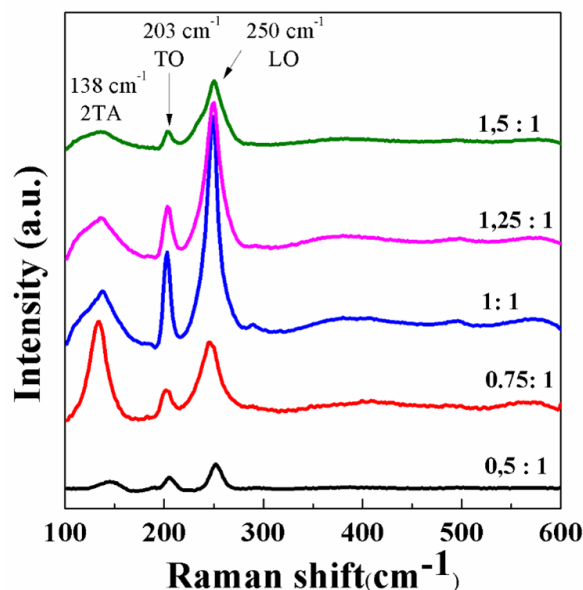
**Fig. 2.** TEM, HR-TEM images and SA-ED pattern of ZnSe NCs with the Zn:Se molar ratio of 1:1. The scale bar is 2 nm.



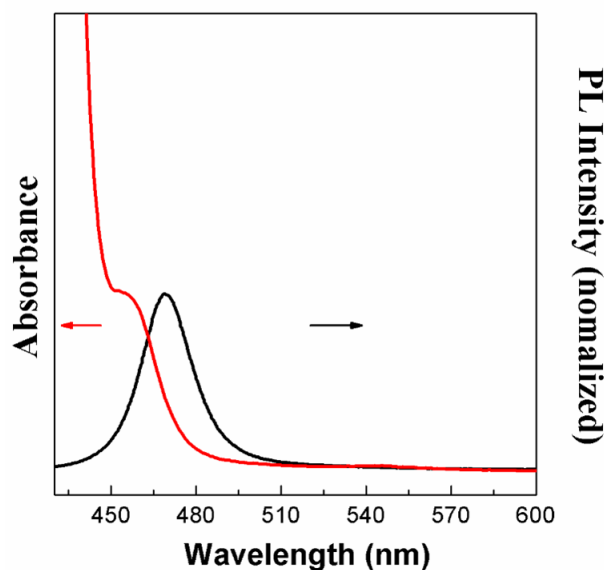
**Fig. 3.** STEM-mapping images of ZnSe NCs with the Zn:Se molar ratio of 1:1.

pattern consists of diffraction dots that are randomly distributed), confirming the good crystalline structure of the synthesized ZnSe NCs. Moreover, the elemental composition was determined in STEM-mapping images of ZnSe NCs (Fig. 3), indicating the existence of Zn and Se without the presence of other elements.

The influences of different synthesis conditions on the formation and quality of ZnSe NCs will be investigated in the following. It is well known that in the synthesis of NCs, the molar ratios of precursors, the growth temperature, and reaction time are the important factors to determine the structural quality and optical properties of the final products [41–43]. In this work, the effect of the reaction temperature was investigated by changing the reaction temperature from 150°C to 200°C while maintaining the duration of growth time of 20 hours and the same Zn:Se molar ratio of 1:1. The XRD patterns taken from all the synthesized samples indicate that the ZnSe NCs have the good crystalline structure as shown above. To determine the effect of the growth duration time, the various syntheses of ZnSe NCs were carried out at the same reaction temperature of 190°C for different times between 5 and 30 hours. The experiments revealed that the particle size of NCs became bigger with increasing growth duration time. NCs prepared for 20 hours are the most uniform and stable. In order to study the influence of the molar ratios of the precursors on the quality of ZnSe NCs product, we employed the Raman spectroscopy as this technique is considered to be a powerful tool to study the microstructure [44, 45] through the lattice vibrations which are related to the local crystalline imperfections or non-stoichiometry in the structures. Fig. 4 shows Raman spectra of synthesized ZnSe NCs with different Zn:Se molar ratios (0.5:1 ÷ 1.5:1). Raman diffraction peaks were observed at 138 cm<sup>-1</sup>, 203 cm<sup>-1</sup> and 250 cm<sup>-1</sup>, corresponding to 2TA, TO and LO phonon modes respectively [46–48]. The absence of Raman mode at 290 cm<sup>-1</sup> may be related to lattice defects [48]. The coexistence of TO and LO modes prove good quality of the synthesized ZnSe NPs, which is in accordance with the results obtained from the above XRD and HR-TEM studies. The quality of luminescence materials, besides their



**Fig. 4.** Raman spectra of ZnSe NCs with different Zn:Se molar ratios.



**Fig. 5.** Absorbance and PL spectra of ZnSe NCs reacted at 190°C for 20 hours with the Zn:Se molar ratio of 1:1.

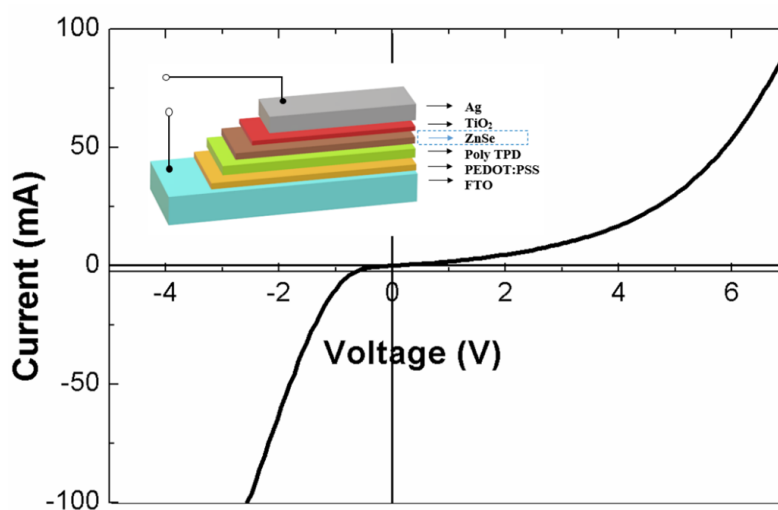
crystalline structure, could be determined by their optical properties. Fig. 5 presents the absorption and PL spectra of ZnSe NCs synthesized at the reaction temperature of 190°C for 20 hours, with the Zn:Se molar ratio of 1:1. The sample is excited by a 355 nm laser. The obtained ZnSe NCs emitted strong blue light at 470 nm with a small full width at half maximum (FWHM) of 16 nm, which is very promising property for further applications in solid-state lighting.

**Table 1.** Report about synthesis methods and selected properties of ZnSe NCs.

Origin	Method	Precursor	Solvent	Ligand	Shape, size	Photoluminescence (PL)
<i>This work</i>	<i>Hydrothermal (120-190 °C, 5-20h)</i>	<i>Zn, Se powders</i>	<i>NaOH</i>	-	<i>Sphere (50-500) nm</i>	<i>Strong (470 nm, FWHM = 16 nm)</i>
Ref. [49]	Hydrothermal (40-180 °C, 2-10h)	Zinc acetate, Sodium selenite anhydrous	NaOH N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	CTAB	Sphere (200-400) nm	N.G.
Ref. [50]	Reverse Microemulsion (RT, oxygen-free by nitrogen)	Zinc acetate, Se powder,	Cyclohexane, NaBH <sub>4</sub>	Triton X-100/2-propanol	Sphere (2.8-14.5) nm	Strong (386-426 nm FWHM = 80 nm)
Ref. [51]	Thermal treatment (450-700°C)	Zinc nitrate, Se powder	PVP, Ethylenediamine	-	N.G. (7-18) nm	N.G.
Ref. [52]	Microwave irradiation (10 <sup>-6</sup> torr)	Zn powder, Se powder	-	-	Sphere (50) nm	Weak (401 nm, FWHM = 50 nm)
Ref. [53]	Hydrothermal (180°C, 12h)	Zinc substrates, Se powder	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O, NaOH	-	Nanowall	N.G.
Ref. [54]	Co-precipitation (8h)	Zinc chloride, Sodium selenide	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O, ethylene glycol, PVP	-	(20-30) nm	Weak
Ref. [55]	Anisotropic growth (240°C, Ar air)	Zinc acetate, Selenium	Oleylamine, octadecene	-	Nanorod (Length: 5-9 nm, d = 2.8)	Strong (396 nm, FWHM = 20 nm)

RT: room temperature, ZB: cubic zincblende, WB: hexagonal wurtzite, d=diameter, N.G.: not given in the article.

Table 1 shows synthesis methods and selected sample properties of ZnSe NCs which are extracted from previous studies. Comparing with those publications, our obtained ZnSe samples were synthesized by simple and low-cost method, with fewer chemicals and less equipment, large-scale of production, and high photoluminescence quantum yield. Moreover, this can be considered as a clean chemical method because the experiment is carried out completely in a closed container. Especially, ZnSe NCs emit strong blue light, promise to be a potential candidate in optoelectronics field, solid-state lighting. To illustrate this capability, we carried out the fabrication of the electronic structure as shown in the inset of Fig. 6 (its details will be presented in the other article) and measured current–voltage (I–V) characteristics. The results of the I–V characteristics of the ZnSe NCs in the built electronic structure show a diode characteristic, which was expectedly used in solid-state lighting and optoelectronic devices.



**Fig. 6.** Current–voltage (I–V) characteristics of the ZnSe NCs.

#### IV. CONCLUSION

The ZnSe NCs were successfully synthesized by the hydrothermal method, using zinc and selenide powders as precursors. The NCs with a 1:1 Zn:Se molar ratio reacted at 190°C for 20 hours were found to show the highest quality. This optimal nanomaterial possesses the high crystal quality and luminescence efficiency, emitting the strong blue light (470 nm), which is desirable for applications in solid-state lighting. The current–voltage (I–V) characteristics of the ZnSe shows its application in solid-state lighting and optoelectronic devices.

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