Zinc Selenide: A Blue Luminescent Nanocrystal

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Abstract: Luminescent nanomaterials possess interesting photo-physical properties along with versatile electrical and mechanical properties. One of the best example of luminescent nanomaterials is, Zinc selenide, ZnSe. ZnSe nanocrystals have wide band gap along with the short wavelength optical path. Thermal and chemical stability make this material a strong contender for applications in high-power operations. This chapter explains the optical and electrical properties of ZnSe and its applications in various sectors. It also represents the properties and different synthesis procedures of ZnSe in detail. The chapter includes and enlightens about the ZnSe nanocrystal as one of the most promising candidate on semiconductor industries.

Keywords: Luminescence; Nanocrystal; Semiconductor; Zinc selenide.

1. Introduction and History of Zinc Selenide (ZnSe)

In the past decade, Semiconductor Nanocrystals have gained attention from the scientific community due to their unique size and tunable optical properties. ZnSe has been a material of choice for blue diode lasers and photovoltaic solar cells. It has a room temperature bulk band gap of 2.7 eV (460 nm). Although Nanocrystals of ZnSe have been produced by an arrested precipitation technique, earlier reports only provided optical absorption spectra without luminescence information. ZnSe has also been used as a capping material on CdSe nanocrystals for surface passivation, but it resulted in marginal luminescence enhancement compared to ZnS. Efforts have been focused on synthesizing ZnSe nanocrystals with luminescent properties from single molecular precursors. However, ZnSe with a relatively high refractive index of 2.4 (at 300 K) might be ideal building blocks for materials with 3D PBG properties [1], [2], [3]. In this study, researchers used the SILAR method to introduce a ZnSe passivation layer in CdSe co-sensitized solar cells. Although this layer wasn't in the ideal form of a conformal overlayer, it still significantly improved the power conversion efficiency when compared to the widely used ZnS passivation layer. The ZnSe layer helped reduce surface charge recombination and enhance light harvesting, leading to improvements in short-circuit current density, open-circuit voltage, fill factor, and photovoltaic conversion efficiency. The efficiency varied with the thickness of the layer, and the highest efficiency of 6.4% was achieved with three SILAR cycle layers. This is almost twice the efficiency of the solar cell without the ZnSe passivation layer. The researchers also fabricated CdSe co-sensitized solar cells with an optimum ZnS passivation layer, but they only achieved a power conversion efficiency of 4.9%, which is much lower than the 6.4% achieved with the ZnSe passivated QDSSCs. This study suggests that ZnSe could be a promising alternative to ZnS as a passivation material [4].

Studies have shown that semiconductor nanoclusters can perform as active layers in optical emission and detection systems. The size of the nanoparticle can be adjusted to modify the optical range of interest. As the size of the particle gets smaller, there is a noticeable shift towards blue in the photocurrent. Hybrid systems made up of different materials, such as nanoparticles or complexes with polymer chains, show various methods for charge production, separation upon optical excitation, and light emission. These systems exhibit intriguing electrical and optical features. Zinc selenide is a crucial direct band gap material, and ZnSe-based laser diodes have been successfully developed to function in a continuous wave (CW) mode at ambient temperature. In contrast to sulfur sources, selenium sources do not exist in many stable phases, so there are few publications on the fabrication of nanocrystalline selenides in the literature. Some common methods for preparing ZnSe nanocrystalline samples include molecular beam epitaxy, metalorganic chemical vapor deposition, and organometallic vapor phase epitaxy [5], [6]. Zinc selenide is a well-known semiconductor of the II-VI type. It is often used in light-emitting devices and is also a popular choice for the window material in thin film solar cells, due to its wide energy band gap. Various techniques are used for producing ZnSe thin films, such as vacuum deposition, chemical vapor deposition, metal-organic chemical vapor deposition, closed-spaced vapor transport, and sputtering. However, electrodeposition has some potential advantages like low-temperature operation, large-area deposition, and relatively low cost. There are several reports on the electrodeposition of ZnSe from aqueous and non-aqueous solutions, as well as from molten salt solutions. By depositing zinc and selenium, ternary compounds such as ZnCdSe or ZnHgSe can be synthesized. Using a flow cell, the deposition of such compounds can be alternated, which creates a superlattice. This technique presents the possibility of deposition composition modulated structures [7], [8], [9].

ZnSe synthesis by Electrochemical Atomic Layer Deposition is a promising proposition. This method uses surface-limited electrochemical reactions, such as underpotential deposition, to create alternate atomic layers of the elements, forming compound layers of compounds. Each deposition cycle forms a monolayer of the compound, and the number of cycles determines the thickness of the deposit. Zinc and selenium can be simultaneously deposited without exceeding the equilibrium potential of either element, thanks to Kroger's theory. This phenomenon is called underpotential deposition and is observed during deposition of zinc and selenium. The deposition potential of zinc is shifted towards positive values due to the Gibbs free energy change of ZnSe formation. A large excess of zinc ions in the solution is required for the ZnSe synthesis process, according to Kroger's model. Proper adjustment of the bath composition should lead to the formation of the stoichiometric compound and may exclude the presence of excess selenium while the solid phase is being formed [10], [11]. Sulfides and selenides are semiconductor materials belonging to the II-VI group and have been extensively studied due to their wide range of applications in light-emitting devices, solar cells, sensors, and optical recording materials. ZnSe, a direct band gap semiconductor, has a room temperature band gap energy and an emission at 2.8 eV, making it suitable for use in photoelectronic devices. Additionally, ZnSe is of great interest for its potential application in optically controlled switching due to its giant photosensitivity. As a result, ZnSe is a popular choice for many forms of applications including thin films, quantum wells, and bulk crystals. Various methods have been employed to synthesize ZnSe nanoparticles, including surfactant-assisted chemistry, a sonochemical method, a solvothermal route, and vapor phase synthesis. Recently, it has been reported that carbon-encapsulated nanocrystalline ZnSe nanoparticles exhibit enhanced blue emission and quenching of orange emission. Lastly, the cytotoxicity of colloidal CdSe and CdSe/ZnS nanoparticles has been studied [12]. Nanometer-sized semiconductor crystals, which are also known as nanocrystals or quantum dots, have been extensively researched to explore their unique properties and potential applications. These materials exhibit interesting behavior due to the confinement of optically excited electron-hole pairs by the crystal boundary. However, a detailed understanding of this phenomenon, known as the quantum size effect, required the development of high-quality colloidal nanocrystals that were uniform in size, shape, crystallinity, and surface passivation. Once such materials became available, significant progress was made in various physical studies. Additionally, the availability of high-quality crystals has led to the development of more complex nanocrystal-based structures, such as quantum-dot solids, light-emitting devices, and even photonic crystals [13], [14].

2. Properties of Zinc Selenide

2.1 Structural Properties

ZnSe thin films were produced at various deposition potentials ranging from -650 to -950 mV versus SCE, with a deposition time and bath temperature of 30 minutes and 75°C respectively. The films analyzed through X-ray diffraction were found to be polycrystalline and have a cubic structure. The diffraction patterns showed crystallographic orientations, including (111), (200), (220), (311), (400), and (331), with peaks observed at angles of 27.25°, 31.43°, 45.10°, 53.65°, 65.71°, and 72.11°, which matched the standard JCPDS card no. 88-2345 for ZnSe. By analyzing the X-ray diffraction patterns, the microstructural parameters were calculated. The crystallite size and micro-strain were obtained from FWHM, which is expressed as a linear combination of contributions from the particle size, D, and strain e. The crystallite size D of the films was calculated from Debye Scherer's formula, which used the FWHM intensity expressed in radians.

$$D = \frac{0.9\lambda}{\beta cos\theta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

The size of the crystallites (D) and the FWHM (b) are related to microstrain, which is caused by lattice misfit. Deposition conditions affect the lattice misfit, and the size of the crystallites can be easily controlled by adjusting the deposition potential. When the deposition potential ranges from -950 to -650 mV versus SCE, the size of the crystallites is between 39 and 44 nm [15]. The HRTEM was used to study the size distribution and morphology of ZnSe nanocrystals. The study involved analyzing ZnSe films of varying thicknesses which included 95 nm, 135 nm, and 230 nm. The 95 nm film was made up of uniformly shaped spherical particles with a narrow size distribution of about 2 nm. This indicates that the film was composed of QDs that were evenly dispersed. In the 135 nm film, the Gaussian fitting of the particle distribution revealed that the particles had an average diameter of 3 nm. When the thickness of the film was increased to 230 nm, the particles were slightly larger, with diameters ranging from 5-11 nm, and an average value of about 8 nm as determined from the Gaussian fitting of the particle distribution. The particle size increased with increasing film thickness, which can be attributed to the enhanced horizontal velocity of adatoms and condensation of energetic Zn and Se vapors. Overall, the size of the particles in the films was comparable to the bulk exciton Bohr diameter of ZnSe (7.8 nm). The HRTEM images also displayed corresponding SAED patterns for different film thicknesses [16], [17].

2.2 Optical Properties

The optical absorption spectra of ZnSe thin films should be examined at room temperature within the range of 350-1000 nm wavelength. As the concentration of zinc acetate increased, the absorption edge shifted towards the lower wavelength side. The calculated absorption coefficient (α) of the films using a specific equation is:

$$\alpha = \frac{2.303A}{t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where A is the absorbance and t is the thickness of the films. The optical band gap Eg has been calculated using the Taucs formula

$$(\alpha h\nu) = B(h\nu\text{-}Eg)n \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where hν is incident photon energy, A is a constant, and the exponent n depends on the type of transition, As ZnSe is a direct band gap material, n =1/2 for the allowed transition. A plot of $(\alpha h\nu)^2$ versus hν shows the linear nature of the plot and shows the existence of direct transitions [18].

2.3 Thermal Properties

Table.1: Thermal Properties of ZnSe

Heat of Formation	422 kJ/mol
Thermal Expansion Coefficient	720 µm/m°C
Specific Heat Capacity	0.339 J/g°C
Thermal Conductivity	14 W/mK

2.4 Mechanical Properties

Table.2: Mechanical Properties of ZnSe

Melting Point	1517°C
Density	5.42 g/cm^3
Youngs Modulus	67.2 GPa
Bulk Modulus	40 GPa
Poisson Ratio	0.28
Knoop Microhardness	1350

2.5 Physical Properties

Table.3 Physical Properties of ZnSe

Density	5.42 g/cc
a Lattice Constant	5.6676 Å
Formula Units/Cells (Z)	4
Molecular Weight	144.35 g/mol

3. Different Synthesis Methods of ZnSe

Zinc selenide is an inorganic compound with the chemical formula ZnSe. It is a solid that appears yellow-orange in color and belongs to the semiconductor family called II-VI. The size of ZnSe particles is typically less than 10nm. As the size of particles reduces, ZnSe NPs exhibit unique properties that differ from that of bulk material. This is due to the quantum confinement effect, where the particle size becomes smaller than the size of the exciton responsible for light emission. The unique properties of ZnSe NPs produce various fluorescence depending on the size of the particle. ZnSe NPs are one of several semiconductor nanoparticles that have gained interest from the scientific community because of their low toxicity and their fluorescence and electronic properties. There are several ways to synthesize ZnSe NPs, such as the microemulsion method, the hot injection method, the ultrasonic-assisted ionic liquid method, and the ultrasonic irradiation method. Wet chemical methods involve using liquid in one of the stages of producing nanoparticles and ultra-dispersed inorganic powders from aqueous and non-aqueous solutions. This method has the unique advantage of producing small grains and forming phases at low temperatures and for a short duration [19]. The equipment and chemicals necessary for the experiment are easily obtainable in a biology or chemistry laboratory. The process requires basic items such as microwave oven machines, mechanical stirrers, and standard laboratory glassware. Chemicals such as Zinc selenite and sodium citrate can be stored in the laboratory without the need for an inert atmosphere. Studies have shown that Zn^{2+} and Cd^{2+} ions can enhance the photoluminescence (PL) intensity of ZnSe NPs by modifying the surface of the particles.

Cd^{2+} and Zn^{2+} nanocomposites emit bright yellow photoluminescence when exposed to ultraviolet excitation of 365 nm from a UV LED in the dark. This can be detected with a better-resolving rate than the previous method [20].

Nanoparticles of ZnSe, measuring approximately 3nm in size, were created using a sonochemical method that involved a solution of selenourea and zinc acetate under argon. This technique is often used to produce unique materials with smaller particles and higher surface areas than other methods. Selenides have many practical uses, such as in thermoelectric cooling, optical filters, solar cells, and sensor and laser materials. The ZnSe nanoparticles were further characterized using various methods, including X-ray diffraction, UV-vis spectroscopy, and transmission electron microscopy [21]. A new method for synthesizing colloidal ZnSe nanocrystals with size-dependent optical properties was also reported. This involved a direct reaction of zinc stearate with selenium dissolved in trioctylphosphine, without the use of pyrophoric reagents. The resulting nanocrystals had tunable photoluminescence in the spectral range of 390-440nm and a constant emission linewidth of 15nm. The growth process was monitored using absorption spectroscopy and could be stopped at the desired size by removing the heating. After cooling, purification of the nanocrystals was achieved by adding methanol and centrifuging. The nanocrystals were then isolated by precipitation with methanol/1-butanol and could be redispersed in various solvents [22].

ZnSe nanostructures were synthesized using the hydrothermal method. There are several other methods used for synthesizing ZnSe nanoparticles, including molecular beam epitaxy, metalorganic chemical vapor deposition, and organometallic vapor phase epitaxy. In recent times, the solvothermal method has gained popularity for its ability to synthesize various nanostructures such as nanotubes, nanorods, nanowires, and nano donuts at low temperatures. One of the major advantages of the solvothermal method is that it can be performed under low pressures and temperatures. However, the use of organic solvents in the process can be harmful to the environment. Therefore, the use of non-toxic solvents is recommended for large-scale production. Different hydrothermal processes have been developed for the preparation of ZnSe nanostructures. The synthesized nanostructure was characterized using various instrumentation techniques. The nanoparticles prepared using CTAB surfactant, with different sources of Zn and Se, were found to be spherical. The results showed that the source of Se did not affect the morphology of ZnSe. The size of the nanoparticles, ranging from 10 to 15 nm, was estimated using Scherrer’s equation [23].

4. Application of ZnSe

LEDs

Solid-state lighting technologies, such as light-emitting diodes (LEDs), have many advantages over traditional incandescent bulbs and fluorescent lamps. They offer greater efficiency, lower power consumption, longer lifespan, and faster response time. Wide-bandgap nanostructures, such as nanodots, nanorods, and nanowires, are showing promise for use in short-wavelength optoelectronic device applications. Recent research has also been conducted on nanoscale light-emitting materials. ZnSe, a wide-bandgap semiconductor with a bandgap energy (Eg) of about 2.7 eV, has potential applications in the UV spectrum of blue (460 nm). Doping is an effective technique to alter the intrinsic features of ZnSe nanostructures by producing new electronic states, which can ease the passage of electrons from one level to a more energetic and less energetic level. Solid-state lighting is an active area of research in generating photometrically high-quality white light while maintaining energy efficiency. White-light emission is particularly desirable for single-component white-light emitters with improved color stability. Recently, LEDs have been developed that exhibit color-saturated deep blue emission centered at 441 nm, with a narrow full width at half maximum of ~15 nm and a maximum luminance of 1170 cd/m^2. This is due to efficient electron injection into the ZnSe/ZnS QDs [24], [25].

Lasers

Optical disk data storage requires lasers that emit short wavelength radiations, especially blue. Researchers focus on developing ZnSe crystals with heavy anions as they have a low-energy optical phonon cutoff, are transparent in a broad spectral range, and reduce nonradiative decay. This makes ZnSe crystals ideal for ZnSe-based lasers. By exciting the sample with 800 nm femtosecond laser pulses, researchers were able to stimulate visible lasing in massive and single nanoribbons using two-photon optical pumping. Before lasing, the ternary nanoribbons' spontaneous emission peak gradually shifted from 422 to 464 nm. However, once the optical pumped energy densities reached the thresholds, nanoribbons showed a tunable up-converted laser emission with a decrease in spectral linewidth. Moreover, wide band gap II-VI compounds-based electron beam-pumped vertical-cavity surface-emitting lasers (eVCSEL) have high power, are easy to manufacture, and are cost-effective. Mg: ZnCdSe:/ZnMgSSe structure achieved one longitudinal mode lasing at 464 nm. Similarly, ZnSSe/ZnMgSSe QW structures grown on GaP obtained lasing in the UV range (377 nm) with an output of 2.8W at RT. Visible semiconductor lasers are commonly used for display applications. They usually utilize second harmonic generation to excite laser diodes (LDs) or injection as a pump source [26], [27].

Photodetectors

Photosensors or photodetectors are devices that use optical and electrical properties to detect radiation. They work by changing electrical conductivity when radiation is absorbed. When light with energy greater than the band gap is absorbed, it changes the number of free electrons and electron holes in the device, leading to an increase in electrical conductivity. Different types of photodetectors are available to suit various applications. For instance, a photodiode or PN diode is made up of an active p-n junction and works under a reverse operational bias. If light falls on the junction, a reverse current flows proportional to the illumination, which can be detected. On the other hand, photoresistors are based on semiconductors like cadmium sulfide (CdS). They are cheaper than photodiodes but are slower, less sensitive and exhibit a strongly nonlinear response. Metal-semiconductor-metal (MSM) photodetectors usually contain two Schottky contacts instead of a p-n junction. They are potentially faster than photodiodes and can have bandwidths up to hundreds of gigahertz. ZnSe, with a bandgap of around 2.70 eV (~460 nm), is a promising material for optoelectronic devices. Compared to Si and GaAs, ZnSe is more sensitive to blue/UV light [28], [29].

Field Emitters

Field emission (FE) is a process that involves injecting electrons into a vacuum from the surface of materials using an electrical field. This process is made possible through the quantum tunneling phenomena. FE has various applications, including high-brightness electron sources, flat panel displays, and microwave devices. The best materials for FE are those that have low work functions and high field-enhancement factors. ZnSe is an excellent candidate for FE, as it has a low work function of 4.84 eV, compared to other common materials like CNTs (5.0 eV), ZnO (5.3 eV), and ZnS (7.0 eV). ZnSe nanoribbon arrays are perfect for FE applications and can be fabricated through the heat treatment of the precursor (ZnSe: 0.38en, where en = ethylenediamine) nanoribbon arrays. After annealing, the nanoribbon morphology is well-preserved, and the crystallinity is significantly improved. The resulting ZnSe nanoribbons are well-aligned, uniformly distributed on the Zn foil substrate, and are single crystals with sharp top ends. At an anode-cathode separation of 100 µm, the FE current density (J) of ZnSe nanoribbon arrays as a function of the applied field (E) is shown in a J-E plot and a $\ln(J/E_2)$-$(1/E)$ plot. The turn-on field at a current density of 0.1 $\mu A/cm^2$ is 5.0 V/µm, and the field-enhancement factor is 1328, which indicates that ZnSe nanoribbon arrays are ideal for FE applications [30], [31].

Sensor

A humidity sensor is an electrical device that detects changes in capacitance or resistance in relation to moisture levels. It is commonly used to measure and report the relative humidity (RH) in the air. The humidity sensor is important in various industries and daily life, especially in monitoring moisture-sensitive environments and detecting trace moisture in pure gases for semiconductor manufacturing, medical, and food applications. Initial research on resistance-based RH sensors using ZnSe nanostructures showed a sensitive response to RH, but lacked stability and reproducibility. However, improvements can be made by using ZnSe nanorod film, which uses molten hydroxides as a reaction solvent without organic dispersant and capping agents. The device has a fitted line equation of RRH = R0 exp(2.07 + 0.10 RH) with a correlation coefficient of 0.993. The response time of the RH device is 50 seconds when RH changes from 20% to 85%, and the recovery time is 81 seconds when RH changes from 85% to 20%. These results indicate that this humidity sensor offers high sensitivity, better stability, and good reproduction [32].

Gas Sensor

Gas sensors that use one-dimensional semiconducting nanostructures are attracting a lot of attention because of their higher sensitivity compared to thin film equivalents. The surfaces of these nanostructures have a rich surface chemistry that can effectively modify the electrical transport properties of the structures due to their high surface-to-volume ratio. ZnSe nanowires have shown dynamic reactions to NO_2 gas under UV light and at ambient temperature. The resistance reached its maximum value as soon as NO_2 was introduced and returned to its initial value once NO_2 was removed. In the dark, ZnSe nanowires have demonstrated reactions to NO_2 concentrations ranging from 50 ppb to 5 ppm, with sensing performance ranging from 101% to 102%. Furthermore, their sensing performance could be enhanced when used at room temperature under UV illumination, from approximately 113% to 234% (50 ppb to 5 ppm NO_2) under UV (365 nm) illumination. In recent years, there has been a growing interest in using photoluminescence for gas detection, mainly due to its unique advantages of remote sensing, distinguishing the gas species, and easy reversion [33], [34].

Solar Cell

Solar cells, also known as photovoltaic cells, are devices that directly convert light energy into electricity utilizing the photovoltaic effect. They belong to the family of photoelectric cells that exhibit different electrical characteristics like current, voltage or resistance when exposed to light. Photoelectric cells generate and support electric current when exposed to light without the need for external voltage sources. The usage of nanostructures like nanowires or nanorods in photovoltaic devices has several benefits, such as allowing for extended absorption paths while maintaining short distances for carrier collection, strong light trapping, and manipulation of material properties. A recent study showcased superstrate-type nano-structured solar cells with ZnSe/ZnO coaxial nanowires embedded in the $CuInSe_2$ (CIS) layer, resulting in a 30% improvement in Jsc. The study produced a ZnSe/CIS heterojunction solar cell with a Voc of 599 mV, Jsc of 11.60 mA/cm^2, and a fill factor of 25.71%, resulting in a conversion efficiency of 1.79%. Wide bandgap materials alone cannot adequately absorb the sun's light. However, the combination of two materials with large bandgaps and type-II band alignment to generate coaxial nanowires may result in a much smaller effective indirect bandgap than either material alone. This can lead to interfacial changes that raise the absorption threshold to a longer wavelength. ZnO/ZnSe core/shell nanowire arrays are projected to display substantial band offsets that restrict carriers. ZnSe quantum dots (QDs) can be used as a dopant in polymer solar cells in an inorganic/organic system with available wavelengths from visible to near-infrared (NIR) regimes. A recent study showed significant enhancement in solar cell efficiency (approximately 5-10%) by first doping Poly (lauryl methacrylate) (PLMA) thin film with Mn: ZnSe QDs and then spin-depositing the film on the surface of an a-Si solar cell under all-solar-spectrum (AM0) conditions [33], [35], [36].

5. Zinc Selenide: a semiconductor fluorescent material

According to H. Morkoc et al. in 1994, research in wide band gaps of semiconductors, specifically ZnSe, has led to significant advancements, making them suitable for device applications. ZnSe, SiC, and GaN have all demonstrated operation in various spectra for optical emitters and detectors. ZnSe leads in laser development with sophisticated designs and improved performance. However, the low damage threshold of ZnSe limits its practical laser applications. GaN is poised to become the semiconductor of choice for short-wavelength lasers in optical memory and other applications. Further development of these materials requires improvement in doping densities and ohmic contact technologies. ZnSe material quality is excellent, but researchers must address the material's short lifetimes to ensure its durability for practical laser applications. The problems related to these materials have shifted from materials science to device development [37]. Margaret A. Hines and Philippe Guyot-Sionnest in 1998 synthesized highly luminescent ZnSe nanocrystals, providing UV-blue nanocrystal materials. Additionally, comparing ZnSe's cubic crystal structure with CdSe's wurtzite structure provides insight into the relationship between structure and electronic properties of the nanocrystals [38].

Zinc selenide (ZnSe) is an important semiconductor belonging to the group II-VI. It has a bulk band gap of 2.67 eV (460 nm) at room temperature, making it a popular material for blue diode lasers and photovoltaic solar cells. The focus of ZnSe synthesis has been mainly on creating luminescent ZnSe nanocrystals from single molecular precursors. However, ZnSe with its high refractive index (2.4 at 300 K) could be an excellent material for creating 3D photonic bandgap (PBG) structures. Monodispersed ZnSe microspheres have not yet been reported, but they could be formed by aggregating small ZnSe nanocrystals. The size of these microspheres can be fine-tuned by controlling the temperature. Optical characterization has revealed that the microspheres exhibit interesting photonic properties. These hollow microspheres, with their tunable interior nanocrystal size, could be inter-incorporated or surface-modified to create novel optical, electronic, and magnetic properties [39]. In 2002, Peter Reiss and his colleagues presented a simple synthetic method for preparing ZnSe core/shell nanocrystals without using any pyrophoric organometallic precursor. Although this method is inefficient, it has proven to be effective in producing fluorescence quantum yields exceeding 80%. Additionally, the luminescence properties of the core/shell nanocrystals are more stable and less sensitive to surface ligand exchange compared to the "bare" core nanocrystals. This is particularly important for the functionalization of nanocrystals before their dispersion in polar media or their grafting to other molecules [40].

In 1991, H. Jeon et al. discovered that laser diode action could occur in blue-green light from quantum wells made of (Zn)Se within ZnSe/Zn(&Se) p-n heterojunctions, even at temperatures up to 250 K. Two different configurations were used, with the GaAs substrate serving as either the n-type or p-type injecting contact. Devices were prepared on both n-type and p-type GaAs epitaxial buffer layers and substrates, which showed output powers exceeding 0.6 W in pulsed operation [41]. In 1996, D.T.F Marple obtained the refractive indexes of ZnSe, ZnTe, and CdTe from prism refraction data and reported them for a range of wavelengths from 2.5 μ to the short-wave transmission limits set by the band gaps. The results were fitted using the standard formula: $n_2=A+[B\lambda_2 / (\lambda_2-c_2)]$, where n is the refractive index and A is the wavelength in microns. For ZnSe, the optimal values of the parameters were found to be A =4.00, B=1.90, and $c_2=0.113$ [42]. In 2000, D.J. Norris demonstrated a simple method of preparing high-quality, highly fluorescent, ZnSe colloidal nanocrystals (or quantum dots) that were doped with paramagnetic Mn^{2+} impurities. Luminescence, magnetic circular dichroism (MCD), and electron paramagnetic resonance (EPR) measurements confirmed that the Mn impurities were embedded inside the nanocrystals. Optical measurements showed that exciting the nanocrystal produced efficient emission from Mn, with a quantum yield of 22% at 295 K and 75% below 50 K. In the MCD spectra, the first excited state's Zeeman splitting was observed to be large (28 meV at 2.5 T) and dependent on doping concentration. It was found to saturate at modest fields. In the low field limit, the effective g factor's magnitude was 430 times larger than in undoped nanocrystals. EPR experiments showed a six-line spectrum, with a hyperfine splitting of 60.4×10^{-4} cm^{-1}, consistent with Mn substitution at Zn sites in the cubic ZnSe lattice [43].

In 2004, Lin Song Li et al. and Kenu-Kyu Song and Seonghoon Lee synthesized monodisperse ZnSe and ZnS nanocrystals in noncoordinating solvents using alternative precursors. They introduced two new concepts, activation of precursors and same injection/growth temperatures, for the growth of ZnSe nanocrystals. They found that the parameter window for the growth of high-quality zinc chalcogenide nanocrystals was narrower than that of the corresponding cadmium chalcogenide nanocrystals. They also discovered that fatty acids were reasonable ligands for the formation of ZnSe and ZnS nanocrystals, unlike synthesis performed in coordinating solvents. Activating the zinc precursor with alkylamines was critical for the formation of high-quality ZnSe nanocrystals. The photoluminescence (PL) quantum yield of ZnSe nanocrystals reached as high as 50%, with a full width of half-maximum as narrow as 14 nm [44],[45]. In 2004, P. Reiss et al. reported a new synthesis method of colloidal ZnSe nanocrystals exhibiting size-dependent optical properties. They prepared the ZnSe quantum dots in a non-coordinating solvent (octadecane) via direct reaction of zinc stearate with selenium dissolved in trioctylphosphine, without the use of pyrophoric reagents. The photoluminescence of the resulting nanocrystals could be tuned in the spectral range 390–440 nm with constant emission linewidths of the order of 15 nm. By surface passivation with larger band gap semiconductors, these ZnSe nanocrystals could be attractive candidates for applications where blue or near UV emitters are needed [46].

The nanocrystal size range depended on the precursor concentration, while their final dimension could be precisely tuned by the reaction time for a given temperature, as the growth rate was relatively slow. In 2013, K. Saikia et al. found that Researchers have found that ZnSe(S) alloyed quantum dots (QDs) exhibit a fivefold increase in photoluminescence compared to native ZnSe nanocrystals. This occurs even without any post-preparative surface treatments under ambient conditions. The team discovered that 3-mercaptopropionic acid (MPA) is the best stabilizer for the ZnSe(S) alloyed system. They found that by incorporating

S2- from MPA after prolonged refluxing time, they could create ZnSe(S) alloyed QDs with low cytotoxicity. The ZnSe(S) system has synergistic enhancement of photoluminescence, dispersibility, and high biocompatibility, making it a novel range of blue-emitting, Zn-based high luminescence QDs. These QDs can be used to develop nano-probes for bioimaging applications. In vitro assays have shown that the ZnSe(S) system has high biocompatibility, which is crucial for its use in medical applications [47]. The article by J.F. Suyver et al. in 2001 discusses the luminescence properties of nanocrystalline ZnSe:Cu as a function of particle size and temperature. The study shows that the emission color of the Cu^{2+} emission is affected by quantum confinement effects and can be altered by changing the particle size. The measurements reveal that both the near band edge ZnSe and the Cu^{2+} emission shift towards a shorter wavelength as the temperature decreases. The temperature dependence is well explained by a theory derived for bulk semiconductors. The shift of the Cu^{2+} emission is attributed to the temperature-induced shift of the conduction band edge. However, the low quenching temperature of the Cu^{2+} emission (~130 K) is a significant limitation for the potential application of ZnSe:Cu nanocrystals in electroluminescent devices [48].

J.F. Suyver et al. 2000 A chemical synthesis method is used to prepare ZnSe nanocrystals doped with Mn^{2+}. Photoluminescence spectra show distinct ZnSe and Mn^{2+} related emissions, both of which are excited via the ZnSe host lattice. The Mn^{2+} emission wavelength and the associated luminescence decay time depend on the concentration of Mn^{2+} incorporated in the ZnSe lattice. The ZnSe-related luminescence has a temperature-induced shift similar to that of bulk ZnSe [49]. Zinc-blende-structured single-crystalline ZnSe nanowires and nanoribbons were grown on (001) silicon substrates through metal-organic chemical vapor deposition by X.T. Zhang et al. in 2003 and Yong-Ji Lee et al. in 2006. Meanwhile, Colloidal CdSe/ZnSe core/shell nanocrystals were prepared using the conventional TOP/TOPO process while controlling their shell thickness by adjusting the ZnSe precursor concentration. The nanowires demonstrated high structural and electronic quality, as evidenced by strong and sharp room-temperature band-edge luminescence. This indicates that metal-organic chemical vapor deposition is a promising method for producing nanoscale optoelectronic devices. The nanowires/nanocrystals were characterized using X-ray powder diffraction and scanning electron microscopy. Their diameters range from a few 10 to 100 nm, while their typical length is in the tens of micrometers. Individual strands of the nanowires/nanocrystals were examined using transmission electron microscopy and cathodoluminescence spectroscopy. They were found to be single crystals elongated along the <112> crystallographic direction. Strong and narrow room-temperature band-gap light emissions suggest that their optical and electronic properties are comparable to those of the epitaxial layers used in diode lasers [50],[51].

Burger et al. 2001 The samples were polycrystalline or single crystals prepared by post-growth diffusion doping or single crystals doped during growth by the physical vapor transport method. Room temperature lifetime values between 6 and 8 µs were measured for samples with Cr^{2+} concentrations from the low 10^{17} to high 10^{18} cm^{-3} range. Lifetime data taken down to 78K was found to be rather a temperature-independent, reconfirming previous reports indicating a quantum yield of the corresponding emission of close to 100% at room temperature. A strong decrease in the room temperature lifetime was found for chromium concentrations higher than 10^{19} cm^{-3} [52]. In 2003, Georgios N. Karanikolos and his team developed a scalable method for synthesizing luminescent compound semiconductor nanocrystals, also known as quantum dots. The process involved using microemulsion-gas contacting at room temperature which allowed for the formation of numerous identical nanoreactors. The team synthesized ZnSe quantum dots by reacting hydrogen selenide gas with diethylzinc dissolved in heptane nanodroplets of a microemulsion formed by self-assembly of a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) amphiphilic block copolymer in formamide. By growing a single nanocrystal in each nanodroplet, the team was able to achieve better control of particle size by manipulating the initial diethylzinc concentration in the heptane. The ZnSe nanocrystals exhibited luminescence that varied in intensity depending on their size and demonstrated excellent photostability [53]. In 2005, Huifeng Qian et al. introduced a new method for quickly synthesizing luminescent ZnSe nanocrystals in an aqueous environment using controlled temperature microwave irradiation. The study systematically investigated the effects of experimental conditions and microwave irradiation on the synthesis of the nanocrystals. The research revealed that the optical properties of the ZnSe nanocrystals were significantly influenced by the pH value of the reaction solution, the molar ratio of precursors, and the duration of microwave irradiation. Within an hour, various nanocrystals of different sizes were created, with the highest photoluminescence quantum yield of 17% achieved under optimal reaction conditions. The nanocrystals demonstrated high crystallinity, as confirmed by HRTEM and XRD analysis. EDS spectra and elemental analysis indicated an increase in sulfur content as the nanocrystals grew, suggesting the structure of an alloy ZnSe(S) shell on the surface of the ZnSe particle core. Additionally, it was discovered that oxygen from the air in the reaction vessel was crucial in decomposing the thiol group under microwave irradiation [54]. In 1984, S Myhajlenko et al. conducted high-resolution luminescence studies on individual dislocations and related defects in ZnSe and InP using a transmission electron microscope. In ZnSe, unusual luminescence bands (Y at 2.60 eV and S at 2.52 eV) that were previously observed in photoluminescence studies are believed to be caused by dislocations. In some cases, the excitonic transitions were completely quenched, which was found to be correlated with the presence of Y emission from complex dislocation tangles. However, for individual screw dislocations, the quenching of the exciton luminescence was found to be variable, and the reduction of the exciton signal was not always observed. On the other hand, no dislocation-related luminescence was detected in InP within the system detection limit (0.7-4.0 eV), unlike in ZnSe [55].

Encai Hao and his team synthesized aqueous suspensions of ZnSe and Cu-doped ZnSe nanoparticles in the presence of mercaptopropionic acid (MPA). The Cu-doped ZnSe nanoparticles exhibited strong blue emission, which was significantly influenced by the Cu dopant level and the chemical surface passivation produced by zinc-mercaptopropionic acid complexes. These Cu-doped ZnSe nanoparticles were then utilized to create ultrathin polymer-supported films using the layer-by-layer assembly method and electrostatic interactions. UV-visible spectroscopy and X-ray photoelectron spectroscopy (XPS) confirmed the presence and optical activity of Cu-doped ZnSe nanoparticles within the polymer ultrathin films. Furthermore, the XPS analysis supported the existence of zinc mercaptopropionic acid complexes on nanoparticle surfaces and the presence of Cu^{2+} ions with high luminescent activity in the doped nanoparticles [56].

6. Recent Research Activities of ZnSe Nanocrystals

Zinc selenide (ZnSe), another well-known direct band gap II–VI semiconductor, which favors absorption over a wide range in the visible spectrum, has been exploited as a potential material. There should be more research activities going on to synthesize ZnSe-based nanocomposites to enhance various properties of it. The heterostructures with limited structural design can also be used in multicomponent devices rather it has been very challenging to synthesize ZnSe-based heterostructure in stable conditions without using any capping agent. More research should be done on the quantum confinement of ZnSe nanocrystals as the organic capping agent has been used to control the size and size distribution. There must be some advancement in enhancing the conduction property of ZnSe quantum dots. The recent advancement of ZnSe nanoparticles and ZnSe-based nanocomposites in solar cells and photodetectors has been tremendous. But it is crucial to examine the optical property of ZnSe nanostructures to enhance their conduction property for solar cells and photodetectors application. It is notable progress, emerging techniques, and implementing potentials of ZnSe nanostructures in various sectors by using its electrical and optical properties. It inspires more research activities in inorganics. Of its prominent semiconductor property, the material has been implemented in cutting-edge technologies like bioimaging, telecommunications, and in military devices.

7. Conclusion

ZnSe nanocrystal is the first fluorescent semiconductor material, which has prominent applications in optoelectronic devices, LEDs, lasers, etc. ZnSe fluorescent semiconductor material provides all the possibilities to analyze the quantum confinement effect. The chapter is concluding the different properties of ZnSe and describes the different application areas. That applications lead research towards the specific electrical sector application based on the thermal stability of crystals. The chapter confines the overall semiconductor property along with using the photophysical property of ZnSe nanocrystals. There has been so much literature on the fabrication of ZnSe-based composite materials which can be implemented in different sectors by either using its optical or electrical properties.

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