

## Review Article

# A Review on the Synthesis Methods of CdSeS-Based Nanostructures

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As typical II–VI ternary alloyed chalcogenides, CdSeS nanostructures have attracted intensive worldwide attention due to their excellent tunable optical properties based on quantum confinement effect and optical nonlinear phenomenon. Because CdSeS-based nanostructures have presented a great potential for applications in biomedicine and optoelectronic devices, different synthesis methods have been proposed to prepare CdSeS-based nanostructures with divergent optical properties to meet the needs of those applications, such as fluorescent labeling, *in vivo* imaging, waveguides, and solar cell. In this review, the tricks, advantages, and disadvantages of all these synthesis methods were discussed, including hot-injection synthesis, one-pot noninjection synthesis, microwave irradiation, solvothermal synthesis, template-assisted electrodeposition, thermal evaporation, and pulsed laser deposition. Special emphasis was put on those methods that are safe, economic, environment-friendly, and suitable for large-scale production of alloyed CdSeS nanostructures with high photoluminescence, high stability, and low/no cytotoxicity.

## 1. Introduction

II–VI compound semiconductor nanostructures have attracted great attention due to their attractive optical and electrical properties [1, 2], presenting new developing direction for fundamental and application-oriented researches [3–6]. As a class of typical ternary II–VI semiconductive compounds, CdSeS alloyed nanostructures [7–13] have been intensively studied because of their fascinating and tunable optical and electrical properties [8, 14] based on quantum confinement effect, such as their tunable band-gaps which can be varied from visible (~2.42 eV for CdS) to near IR (~1.73 eV for CdSe) [14]. And their excellent optical properties such as large nonlinear susceptibilities, fast response times, and good photoconduction [15, 16] provide them with a wide range of potential applications in biomedicine [17–19] and optoelectronic devices [20–25]. In particular, those alloyed CdSeS nanostructures with high quantum efficiency, narrow spectral emission, wide band-gap energy, and easy color tunability are very good candidates for the next-generation optoelectronic and biomedical applications

[19, 26, 27], such as solar cell, fluorescent labeling, *in vivo* imaging, biosensors, and drug delivery. Consequently, the preparation of CdSeS nanostructures with excellent quality to satisfy the requirements of future applications is becoming more and more essential.

In the recent decades, many different synthesis methods for CdSeS nanostructures were proposed. They all have their own features and the resultant CdSeS nanostructures also have different morphologies and properties. To obtain CdSeS nanostructures with special properties suitable for specific application, the understanding of their synthesis methods is necessary, which is also conducive to develop some new ways to realize the controllable growth of CdSeS nanostructures. Thus in this paper, the existing synthesis methods of CdSeS nanostructures, including hot-injection synthesis, one-pot noninjection synthesis, microwave irradiation, solvothermal synthesis, template-assisted electrodeposition, thermal evaporation, and pulsed laser deposition, are reviewed. The advantages and disadvantages of these synthesis methods were discussed in detail. Special emphasis was put on those methods that are safe, economic, environment-friendly, and

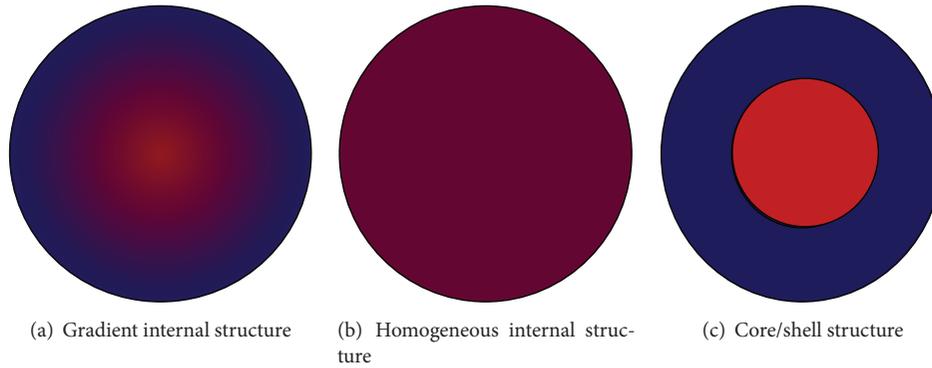


FIGURE 1: A schematic representation of three typical CdSeS quantum dots.

suitable for large-scale production of alloyed CdSeS nanostructures with high photoluminescence, high stability, and low/no cytotoxicity.

## 2. The Development History of CdSeS-Based Nanostructures

To date, there are many kinds of CdSeS-based nanostructures prepared by different synthesis methods, including nanostructures in zero-dimensional (0D, quantum dots, QDs, or nanocrystals), one-dimensional (1D, nanowires, whiskers, nanorods, nanoribbons, or nanobelts), and two-dimensional (2D, nanofilms or nanosheets) and CdSeS-based nanocomposite structures. These different forms of CdSeS nanostructures all have their own special properties and applications.

**2.1. Zero-Dimensional CdSeS Nanostructures.** Zero-dimensional CdSeS nanostructures have the advantages of not only high luminescent efficiency, color monochromaticity, and facile band-gap tunability in visible light region for making light-emitting diodes (LEDs) [28] to replace the conventional inorganic- or organic-based LEDs and applying to QDs-sensitized solar cells [16], but also high brightness, broad absorption and sharp emission spectra, tunable emission maxima, and longer fluorescence lifetime to be used for fluorescent labeling [29], *in vivo* imaging [30, 31], photovoltaics [32], and other applications [33, 34]. For CdSeS QDs or nanocrystals, band-gap engineering can be achieved via the control of their sizes, constituent stoichiometries, and internal structures (such as homogeneous versus gradient) [35]. The homogeneous CdSeS QDs have a uniform internal structure; thus the composition is the same everywhere on a single quantum dot, while in gradient CdSeS QDs, alloy compositions are varied radially; namely, the ratio of S and Se changes gradually from the core to surface of the QDs in a gradient internal structure. But unlike traditional core@shell structures, in such gradient internal structure there is no abrupt boundary between the Se-rich core and S-rich shell [36]. The as-described three structures of CdSeS QDs can be shown in Figure 1. The gradient alloy nanocrystals present optical properties that are significantly different from those of the homogeneous alloys [37]. To achieve homogeneous

alloys, the growth rates of the two constituent materials must be equal [12, 37], and the conditions necessary for the growth of one constituent cannot impede the growth of the other [38]. And CdSeS QDs with different internal structures can be prepared through the same synthesis methods by using different selenium and sulphur precursors [36]. Because the band-gap can be tuned by adjusting sizes, constituent stoichiometries, or internal structures, CdSeS QDs or nanocrystals with tunable optical properties would be obtained even in a constant size, which have promising applications in special field. For example, in *in vivo* imaging, very small CdSeS QDs with a certain size, which can achieve a range of fluorescence colors, are desired.

Various CdSeS QDs or nanocrystals were prepared successfully by different synthesis methods. As early as in 2001 [39], Elbaum et al. prepared  $\text{CdSe}_{1-X}\text{S}_X$  ( $0 < X < 1$ , the same below) crystals with a size distribution varied between 5 and 10 nm by a precipitation method. However, this method usually leads to crystals with surface properties that can vary considerably. But, for nanocrystalline semiconductors with very large surface-to-volume ratio, their properties are normally very sensitive to surface effects [40]. Then, in 2003 [12], Jang et al. prepared highly luminescent CdSeS QDs via a rapid hot-injection synthesis method, and the resultant CdSeS QDs have quantum efficiency up to 85% and the full width at half maximum (FWHM) of photoluminescence peaks was about 34 nm, which can present tunable luminescence properties from red to blue region. Meanwhile, the authors also claimed that it was hard to judge the structure of their QDs to be either core/shell or gradient. In 2005 [41], Qian et al. presented a seed-mediated approach for rapid synthesis of high quality alloyed QDs (CdSe-CdS) in aqueous phase by microwave irradiation. Although the QDs prepared in aqueous phase have excellent water solubility, stability, and biological compatibility, their quantum yield is usually very low due to the serious traps on their surface. In 2006 [38], Swafford et al. fabricated alloyed  $\text{CdSe}_{1-X}\text{S}_X$  QDs with homogeneous internal structure in all proportions by means of pyrolytic synthesis based on a swift hot-injection method, and they reported that the morphology of the resultant nanocrystals can be altered by changing the reaction conditions, generating structures ranging from homogeneous, spherical nanocrystals to one-dimensional

gradient nanorods. But these QDs also exhibited significant deep-trapping emission, causing decreased quantum yields, and this method is unsuitable for large-scale production and is not ecofriendly because it employed organic compound containing phosphine. In 2009 [35], a noninjection, one-pot approach with excellent synthetic reproducibility was reported to fabricate homogeneously alloyed CdSeS nanocrystals by Ouyang et al. And the resultant CdSeS QDs can be tuned easily to emit photons in the range of 470–550 nm of the electromagnetic spectrum. This method is a green approach with the avoidance of phosphines, but the quantum yield was below 5%, and it is worth noting that 2,2'-dithiobisbenzothiazole was used as nucleation initiator during synthesis and the nucleation initiator was the key to successfully prepare high quality quantum dots [42]. To make the method greener, in 2010 [43], Zou et al. prepared alloyed CdSe<sub>1-x</sub>S<sub>x</sub> QDs with high monodispersity and narrow size distribution by a noninjection method without nucleation initiators. However, the quantum yield was still quite low. In 2013 [44], Ünlü et al. proposed a two-phase thermal approach to prepare CdS<sub>x</sub>Se<sub>1-x</sub> ternary nanocrystals without injection, resulting in highly luminescent CdSe<sub>1-x</sub>S<sub>x</sub> nanocrystals with a high quantum yield of about 90% at low temperature, but, in this approach, the organic compound containing phosphine was also employed. In a word, it is a trend that the synthesis methods of 0D CdSeS nanostructures gradually shift from hot-injection to noninjection based ones. And new facile, green synthesis methods suitable for large-scale production of CdSeS QDs or nanocrystals are expected.

**2.2. One-Dimensional CdSeS Nanostructures.** One-dimensional CdSeS nanostructures have received considerable attention because of their special properties [45–51], such as dimensionality confined transport phenomena [51] and continuously tunable physical properties through the control of their compositions [48]. Consequently, they have shown great potential as the building blocks for new, nanoscaled electronic, and optoelectronic devices [52–54], for example, waveguides [20], lasers [55, 56], field-effect transistors [13], photosensor [57], photovoltaic cells [58], and photodetectors [59]. To apply the nanostructures in these applications, it is essential to synthesize 1D CdSeS nanostructures with controllable compositions and tunable physical properties. On the other hand, preparing CdSeS nanowires or nanobelts with tunable band-gap is important for investigating the mechanism of free carrier and electron-hole dynamics based photoconductivity and charge transport in 1D CdSeS nanostructures.

To date, 1D CdSeS nanostructures with different morphologies and properties have been fabricated by various synthesis methods. In 1999 [60], Yu et al. successfully prepared CdSe<sub>1-x</sub>S<sub>x</sub> nanowires by a low-temperature solvothermal route, and the morphology of the obtained CdSe<sub>1-x</sub>S<sub>x</sub> nanocrystallites could be well controlled by choosing an appropriate solvent. Through the same method, in 2006 [61], Liu et al. synthesized CdSe<sub>1-x</sub>S<sub>x</sub> nanorods with diameter of 10–20 nm and length up to 100–150 nm. The CdSe<sub>1-x</sub>S<sub>x</sub> nanorods could be obtained at a temperature as low as 120°C and the size distribution of the obtained nanorods would

not change with temperature and composition. Although the reaction temperature is relatively low in solvothermal synthesis, it needs long reaction time (usually more than 10 h) and the products need to be washed for many times by different solutions. In 2005 [62], alloyed ternary CdSe<sub>1-x</sub>S<sub>x</sub> nanowire arrays with continuous tuning of the band-gap through composition modulation were prepared by Liang et al. via an anodic aluminum oxide template-assisted electrodeposition method. But this method is energy-wasting due to the fact that the preparation was carried out under dc deposition conditions. In the same year [8], Pan et al. fabricated sword-like CdSe<sub>1-x</sub>S<sub>x</sub> nanobelts with color-tunable photoluminescence and site-controlled compositions via a simple physical evaporation process with Au catalyst. The nanobelts have a typical length of 20–60 μm and a thickness of 40–80 nm, and the width of the nanobelts is 100 nm to 1 μm at one end and tapers off to approximately 50–100 nm tip at the other end. And, later in 2006 [20], the same group of authors prepared single-crystal ultralong alloyed CdSe<sub>1-x</sub>S<sub>x</sub> whiskers through the similar Au-catalyzed thermal evaporation route. Moreover, in 2005 [63], Kwon et al. reported a pulsed laser deposition with Au catalyst to synthesize CdSe<sub>1-x</sub>S<sub>x</sub> nanowires, and the intensity of the optical luminescence of the obtained nanowires showed a quadratic relationship with their composition. However, in both thermal evaporation and pulsed laser deposition, due to the sensitivity of nanostructure composition to the local substrate temperature during the growth process, the products of different compositions with variable X are typically codeposited on a single substrate, and the composition X changes with the distance of the substrate from the evaporation sources. In other words, the uniformity and selectivity of stoichiometry of the nanostructures cannot be ensured. So, the synthesis methods to obtain ternary CdSe<sub>1-x</sub>S<sub>x</sub> with uniform and controllable compositions are desired. In 2009 [54], Li et al. prepared CdSe<sub>1-x</sub>S<sub>x</sub> nanoribbons via sulfurizing CdSe nanoribbons, and the obtained products presented tunable and sharp near-band-gap emissions and lasing action from 542 to 668 nm. It is the first time that 1D ternary CdSe<sub>1-x</sub>S<sub>x</sub> single-crystal nanoribbon with uniform and controllable compositions was prepared. But a H<sub>2</sub>S-Ar atmosphere was used during this sulfurizing process. It is not environment-friendly. In 2011 [13], Lu et al. synthesized CdSe<sub>1-x</sub>S<sub>x</sub> nanobelts with accurately controllable compositions by a thermal evaporation method with a specially designed substrate holder. In recent years, more and more synthesis methods were proposed to prepare different 1D CdSeS nanostructures with excellent tunable optical and photoelectrical properties, and it is essential to develop simple and facile method to synthesize 1D ternary CdSeS nanostructures with uniform composition on large scale.

**2.3. Two-Dimensional CdSeS Nanostructures.** Compared with abundant literatures on 0D and 1D CdSeS nanostructures, there are only few reports on 2D CdSeS nanostructures. It is short of literatures reported on CdSeS 2D nanostructures (for instance, nanosheets and nanofilms) possibly because it is very difficult to maintain the 2D morphology of the nanostructures while precisely controlling the thickness at

atomic level during the synthesis. But such materials are of great importance for their many applications such as solid-state lighting, high efficient solar cells, discrete multicolor lasers, and multispectral detection [64, 65], owing to their wide tunable band-gaps, low surface activity, and good photoconductive and photoluminescent properties [66–68]. In 2009 [69], Kim et al. reported lateral heterostructure CdSeS nanosheets, which were synthesized by a physical vapor transport process, and strong red and green emissions could be observed by selective laser excitation focusing at the center and edge parts of these heterostructure nanosheets, respectively. However, nanosheets show a strong suppression effect of S incorporation during the growth dominated by the vapor-solid mechanism; namely, a strong preference for the incorporation of Se species may exist in the competition between S and Se species migrating toward the  $\pm(0001)$  side surfaces. So, CdSSe nanosheets with very small level of S incorporation resulted even if a sufficient amount of S vapor is transported. So, it is of no benefit to the synthesis of CdSSe nanosheets with varied compositions for band-gap engineering. Then in 2014 [65], Maiti et al. reported a solution phase synthesis method to prepare homogeneous ultrathin alloyed  $\text{CdSe}_{1-x}\text{S}_x$  nanosheets, and the optical properties of the resultant  $\text{CdSe}_{1-x}\text{S}_x$  nanosheets showed a comparable or higher quantum yield with those of pure nanosheets. But stacking faults were detected in these CdSeS nanosheets, which may affect the optical properties of CdSeS nanosheets. Consequently, more novel delicate and low cost synthesis methods on 2D CdSeS nanostructures are needed to develop.

**2.4. CdSeS-Based Nanocomposite Structures.** CdSeS nanocomposite structures mainly exist in the form of radial core/shell heterostructures. The presence of such nano-sized heterointerface between semiconductor shell and core provides significant advantages for both light absorption and charge separation. And they have exhibited diverse applications in field-effect transistor, solar cells, light-emitting diodes, high electron mobility devices, and memory devices [70–76]. In 2007 [77], Chong et al. prepared  $\text{TiO}_2$  nanobelts/CdSeS QDs nanocomposite structures, and the corresponding visible light sensitizing effect shows a 3- to 4-fold increase in photocurrent in the coupled system. In 2008 [75], Pan et al. synthesized uniform  $\text{Si@CdSeS}$  core-shell nanowires with continuously tunable light emission in the visible region by thermal evaporation method. And these kinds of nanostructures may have potential applications in multicolor nanoscaled light-emitting devices. In 2010 [74], Myung et al. fabricated vertically aligned and composition-tuned  $\text{ZnO@CdSSe}$  core-shell nanowire arrays by chemical vapor deposition on pregrown ZnO nanowire arrays, which was a Zn containing alloy formed in the interface region between the ZnO core and shell, facilitating the growth of single-crystalline shell layers by reducing both the lattice mismatch and the number of defect sites, thus resulting in higher photoelectrochemical cell performance of the  $\text{ZnO@CdSSe}$  core-shell nanocables. In 2012 [76], Qin et al. reported stable  $\text{CdSeS@ZnS}$  core-shell colloidal QDs suitable for single dot imaging, and, compared with  $\text{CdSe@ZnS}$  core-shell QDs

with similar core size, the biexciton recombination rate and electron confinement energy are both smaller by about 40% in  $\text{CdSeS@ZnS}$  core-shell QDs. CdSeS nanocomposite structures combine the advantages of alloyed CdSeS nanostructure and its composited components. They have unique properties, which cannot be obtained from their individual component. So they can be used for some special applications like cancer diagnosis [78] through modification and conditioning. Therefore, the preparation of CdSeS nanocomposite structures is of great significance.

### 3. Synthesis Methods of CdSeS-Based Nanostructures

**3.1. Hot-Injection Synthesis.** Hot-injection synthesis is a very facile and useful method to prepare CdSeS nanostructures with high luminescence, which is also called organometallic high-temperature colloidal method [79]. Generally, there are three main steps in hot-injection synthesis. First, one should prepare a Cd precursor at elevated temperature under inert gas flow, in which the solvents are usually organic compounds. Second, a fresh Se and S mixed precursor solution with a fixed molar ratio should be prepared. Using different Se and S precursors and controlling their relative amounts can tune the internal structures of CdSeS nanostructures [36]. In the third step, the freshly prepared Se and S mixed precursor is rapidly injected into the hot Cd precursor under vigorous stirring, and then, by controlling the reaction time and temperature strictly, CdSeS nanostructures with different morphologies and properties can be obtained. Utilizing this hot-injection synthesis, CdSeS QDs with tunable luminescence properties were prepared for the first time in 2003 [12]. After that, many kinds of CdSeS nanostructures were prepared by this method or its variant with a little modification. Some typical CdSeS nanostructures prepared by such method are summarized in Table 1. From this table, it can be seen that, by employing hot-injection synthesis method, many forms of nanostructures, such as CdSeS QDs, nanocrystals, nanowires, nanorods, and nanocomposite structures could be fabricated, but in most of the cases this method is to prepare CdSeS QDs.

The as-described three steps are all crucial for hot-injection synthesis. The solvents, Se and S precursors, ratio of Se and S, reaction time, and temperature all have an important effect on the physical and optical properties of the prepared CdSeS nanostructures and even on the success in the preparation. For example, in 2007 [88], Al-Salim et al. systematically studied the effect of solvents on CdSeS nanocrystals prepared by hot-injection synthesis. They chose eight different solvents from coordinating to noncoordinating ones. The results indicated that the type of solvents played a significant role in developing the crystal phase, composition, size, shape, and optical properties of CdSeS nanocrystals. For details, please check Table 2.

Usually, in hot-injection synthesis, the solvents are organic compounds, and the capping agents are often chain organic compounds containing phosphine (such as trioctylphosphine and tributylphosphine). However, these organic compounds are often toxic, unstable at high temperature, and expensive.

TABLE 1: Different CdSeS nanostructures prepared by hot-injection synthesis.

The resulting nanostructure	Cd precursor	Se/S precursors	Reaction parameters	Crystalline structure	Quantum yield	Refs.
CdSeS QDs	CdO + oleic acid	Trioctylphosphine Se + trioctylphosphine S	300°C, 10 s~4 min	No data	85%	[12]
CdSe <sub>1-x</sub> S <sub>x</sub> nanocrystals	CdO + oleic acid	Tri-n-butylphosphine Se + tri-n-butylphosphine S	315°C, <15 min	Zinc blende	1~30%	[41]
CdSeS QDs	(CH <sub>3</sub> COO) <sub>2</sub> Cd + oleic acid	Trioctylphosphine Se + trioctylphosphine S	230~300°C	Wurtzite or zinc blende	30~80%	[79]
CdSe <sub>1-x</sub> S <sub>x</sub> QDs	CdO + oleic acid	Trioctylphosphine Se + trioctylphosphine S	300°C, ~4 min	Zinc blende	No data	[80]
CdSeS QDs	CdO + oleic acid	Tri-n-butylphosphine Se + tri-n-butylphosphine S	275~290°C	No data	No data	[81]
CdSeS QDs	CdO + oleic acid	Trioctylphosphine Se + trioctylphosphine S	300°C, 1 min	No data	40~60%	[27]
CdSeS/ZnS QDs	CdO + oleic acid	Trioctylphosphine Se + trioctylphosphine S	280°C, 1 min	No data	No data	[82]
CdS <sub>1-x</sub> Se <sub>x</sub> nanorods	CdO + octadecylphosphonic acid	Trioctylphosphine oxide Se + trioctylphosphine oxide S	315°C	Wurtzite	No data	[83]
CdSeS/ZnS QDs	CdO + oleic acid	Trioctylphosphine Se + trioctylphosphine S	280°C, 4 min	Zinc blende	14~20%	[76]
CdSeS nanocrystals	CdO + oleic acid	Trioctylphosphine Se + trioctylphosphine S	300°C	Zinc blende	No data	[84]
CdSeS QDs	CdO + oleic acid	Tri-n-butylphosphine Se + tri-n-butylphosphine S	220°C, 2 h	Zinc blende	67%	[85]
CdSeS QDs	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O + polyethylene glycol	Na <sub>2</sub> SeO <sub>3</sub> + Na <sub>2</sub> S + 3-mercaptopropionic acid	80~260°C	Zinc blende	49%	[86]
CdSeS nanowires	CdO + oleic acid	Trioctylphosphine Se + trioctylphosphine S	300°C, 2 min	Wurtzite	No data	[87]

TABLE 2: CdSeS nanocrystals synthesized in different solvents by hot-injection synthesis [88].

	Solvents	Crystal size (nm)	Crystal phase	Influence
Coordinating	Trioctylphosphine oxide (TOPO)	2.5–4.5	Hexagonal	As potential ligands to chalcogen sites, they can activate the crystal surface along the <i>c</i> axis
	Trioctylphosphine (TOP)	3.5 × 6	Hexagonal	
	Oleylamine (OLA)	3.7 × 8	Hexagonal	
	Hexadecylamine (HDA)	No data	Hexagonal	
Weak or noncoordinating	Trioctylamine (TOA)	4–8	Cubic	Surface capped with oleic acid
	Dioctylamine (DOA)	5	Cubic	
	1-Octadecene (ODE)	5	Cubic	
Nonsurfactant	Triphenylphosphine (TPP)	9	Hybrid phase	Hexagonal/cubic phases

Thus, solvents which are less toxic, more stable at high temperature, and relatively cheaper are desired. In [86], glycerin was tried as a stabilizing agent replacing tri-*n*-octylphosphine oxide (TOPO) to fabricate CdSeS nanocrystals in cubic structure.

Hot-injection synthesis can prepare CdSeS nanostructures with tunable photoluminescence emission wavelength and narrow size distribution for many applications. However, the main drawback with it is the requirements of rapid injection and subsequently fast cooling. It is not easy to realize in industrial production. Consequently, hot-injection synthesis is not suitable for large-scale production. In addition, it performs poorly in synthesis reproducibility [35].

**3.2. One-Pot, Noninjection Synthesis.** One-pot, noninjection synthesis overcomes the disadvantages of hot-injection synthesis. It does not need to inject precursor solution rapidly and decrease the reaction temperature in a very short time. The main procedure of one-pot, noninjection synthesis is summarized below. First, one should prepare a Cd precursor in an organic system and prepare a Se and S precursor in organic or inorganic system (sometimes, just Se and S powders) under inert gas protection. Then, the two precursors are mixed in a designed proportion at a proper temperature and react at a selected temperature under inert gas flow. Finally, the resultant products are purified (usually washing and centrifuging for several times).

In 2009 [35], Ouyang et al. reported the method of one-pot, noninjection synthesis to prepare homogeneously alloyed CdSeS QDs with a cubic crystal structure, in which 2,2'-dithiobisbenzothiazole (MBTS) was used as nucleation initiator. The resultant CdSeS QDs could be easily tuned to emit photons in the range of 470–550 nm (see Figure 2 [35]) with a fixed Cd/Se/S feed molar ratio but different S/MBTS feed molar ratios. Such an emission window is hard to achieve within binary CdS and CdSe QDs alone [42]. In this method, Cd/Se/S and S/MBTS feed molar ratios affected the growth kinetics of the resultant QDs as well as their compositions, which determine the band-gap mainly. The higher the Cd/Se/S and the lower the S/MBTS feed molar ratios, the lower the band-gap of the resultant CdSeS QDs. But the nucleation initiators are often toxic and expensive. So, in 2010 [43], Zou et al. proposed an improved

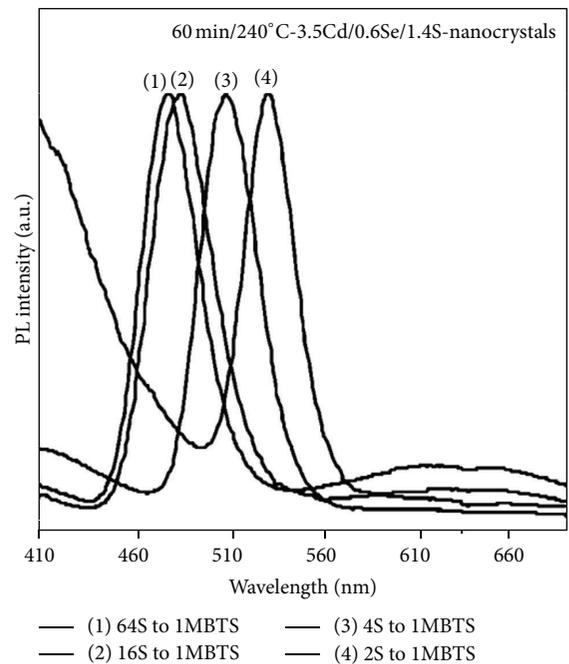


FIGURE 2: The normalized photoemission spectra of CdSeS QDs with a fixed 3.5Cd/0.6Se/1.4S feed molar ratio but different S/MBTS feed molar ratios prepared by one-pot, noninjection synthesis [35].

one-pot, noninjection synthesis method. They fabricated alloyed CdSe<sub>1-x</sub>S<sub>x</sub> QDs with tunable band-gap energy by adding oleic acid (OA) into the reaction mixture without any nucleation initiators, and the microstructure examination verified that highly monodispersed nanocrystals with narrow size distribution were obtained for the samples with all the molar ratios of S to Se, which can be seen in Figure 3 [43]. OA accelerated the nucleation just as the nucleation initiators do, and the difference is that OA increased the reactivity of Cd precursors while MBTS increased the reactivity of S. On the other hand, OA stabilizes the further growth of CdSeS nanocrystals. But the quantum yields of the CdSeS QDs obtained from the as-described two works are very low (below 5%). In 2013 [44], Ünlü et al. prepared highly luminescent CdSe<sub>1-x</sub>S<sub>x</sub> QDs with high quantum yields (up to 90%) via a one-pot, noninjection synthesis with further but

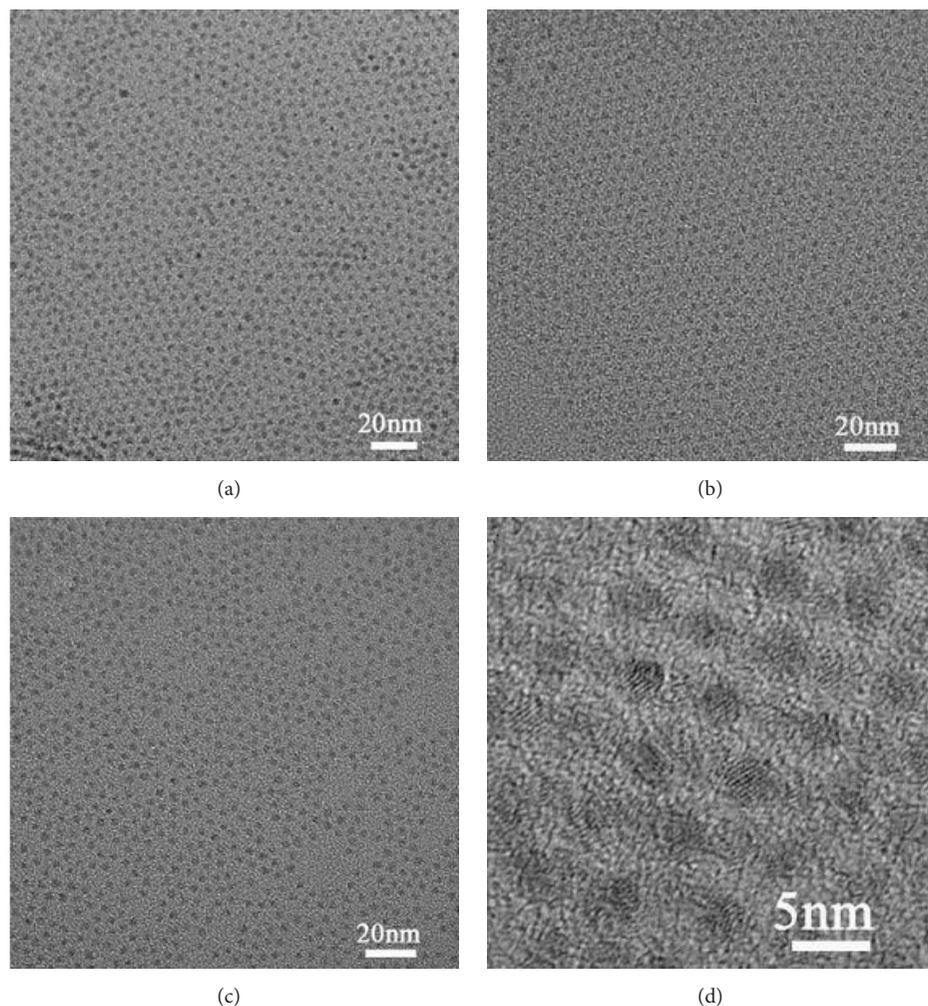


FIGURE 3: Transmission electron microscopy images of the CdSeS nanocrystals prepared at 240°C with different Se/S feed molar ratios: (a) 1/3, (b) 1/1, and (c) 3/1. (d) High-resolution transmission electron microscopy image of the CdSeS nanocrystals shown in (b). They were prepared via the improved one-pot, noninjection synthesis without any nucleation initiators [43].

still slight modification. They also called their method two-phase thermal approach. In the synthesis process, organic Cd precursor and aqueous Se and S precursors were employed, and the hydrodynamic size of the obtained  $\text{CdSe}_{1-x}\text{S}_x$  QDs could be varied from 1.4 to 10.0 nm with the reaction time. The CdSeS QDs formed at the interface of the two liquid phases, and the internal structure of the nanoalloys varies with the initial molar ratio and the reactivity of chalcogenides towards cadmium ions. But, before that, CdSeS QDs with composition gradient and homogeneous internal structures have also been successfully prepared in aqueous solution by using different Se and S precursors, because different Se and S sources could release selenium and sulphur ions at different rates or have different reaction rates of selenium or sulphur toward cadmium [36]. Then, in 2014 [89], employing one-pot, noninjection synthesis method with some modifications, Jia and Tian prepared  $\text{CdSe}_{1-x}\text{S}_x$  QDs in liquid paraffin with a fluorescence emission covering the entire visible region from violet to red. Moreover, homogeneous, ultrathin alloyed  $\text{CdSe}_{1-x}\text{S}_x$  nanosheets with a typical width of 20–40 nm and

length of several hundred nanometers were also prepared by this method [65].

One-pot, noninjection synthesis is an easy handling method, featuring in large-scale production with excellent synthesis reproducibility. But to obtain high quality CdSeS nanostructures with high quantum yield, more modifications are still needed in the synthesis process.

**3.3. Microwave Irradiation.** Microwave irradiation creates friction and collision of molecules at high temperature to decompose chemicals. It is a useful synthesis method in aqueous phase and works with the help of a microwave digestion/extraction system equipped with some exclusive Teflon inner vessels. In 2005 [41], utilizing microwave irradiation, Qian et al. synthesized alloyed gradient CdSeS QDs with good optical properties by using oxygen-free NaHSe solution and  $\text{CdCl}_2/3$ -mercaptpropionic acid (MPA) mixed solution as Se and Cd precursor, respectively. During the synthesis, MPA also released sulfide ions in aqueous solution gradually. Later, another group of authors also prepared

CdSeS QDs composed of a CdSe-rich core and thick CdS shell with homogeneous size distributions in aqueous phase via microwave irradiation [90, 91]. The physical properties of some typical CdSeS QDs prepared by microwave irradiation are shown in Table 3.

Typical procedure of microwave irradiation synthesis is as follows. Firstly, a precursor solution containing tunable molar ratio of Cd:MPA:Se was first adjusted to an appropriate pH (usually, 9~9.5). Then, a certain amount of the precursor solution was sealed in an exclusive vessel and heated inside a microwave digestion furnace via microwave irradiation. After the reaction was completed, the solution was cooled down to ambient temperature naturally. The detailed reaction conditions for typical cases could be seen in Table 4. Typically, the CdSeS QDs fabricated by the microwave irradiation had a gradient internal structure with CdSe-rich core and CdS-rich shell, which resulted from their formation mechanism under microwave irradiation as schematically shown in Figure 4 [41]. At the initial stage, only CdSe monomers nucleated and grew because few  $S^{2-}$  anions were released by the decomposition of MPA at low temperature. As the temperature increased under microwave irradiation, a large number of MPA were decomposed into  $S^{2-}$  anion. At this stage, tiny CdSe monomers mentioned above served as seeds (the existing of CdSe seeds was very crucial for the synthesis of high quality QDs), and the released  $S^{2-}$  anion began to participate in the growth of CdSe nanocrystals. Finally, alloyed CdSeS QDs formed. The bias molar ratio of  $Cd^{2+}:Se^{2-}:S^{2-}$  and the difference in the intrinsic reactivity of S and Se with cadmium would result in the formation of QDs with a gradient alloy structure. During the synthesis, the initial core was rich in Se due to the faster reaction of Se with cadmium. As the free CdSe monomers were depleted from the reaction mixture, the crystal growth mainly contributed to CdS deposition. Finally, alloyed QDs with a gradient Se concentration from the core to the surface were formed.

Comparing with conventional hydrothermal synthesis, the synthesis of nanocrystals by microwave irradiation is generally quite faster, simpler, and very much energy efficient [92, 93]. However, the mechanism of thermal effects and nonthermal effects of microwave irradiation has been poorly understood, limiting to some extent the use of microwave irradiation.

**3.4. Solvothermal Synthesis.** Solvothermal synthesis is a method in which poorly soluble or insoluble reactants were dissolved in a special sealed reactor (autoclave) under a relatively high temperature and high pressure reaction environment, and the solvent is organic or nonaqueous. Then a new material was formed by reacting and recrystallizing in this organic or nonaqueous reaction system.

Using solvothermal synthesis, 1D CdSeS nanostructures with different morphologies and physical properties have been fabricated. In 1999 [60], CdSe<sub>1-x</sub>S<sub>x</sub> nanowires were successfully prepared via the solvothermal synthesis in ethylenediamine (en). CdC<sub>2</sub>O<sub>4</sub> as Cd source, S powder as S source, and elemental Se as Se source in an appropriate ratio were put into a stainless steel autoclave filled with ethylenediamine up to its 80% capacity. And the autoclave

TABLE 3: The physical properties of CdSeS QDs prepared by microwave irradiation.

System	Internal structure	Size (nm)	Quantum yield	FWHM (nm)	Refs.
CdSeS QDs	Gradient	12	~25%	28	[41]
CdSeS QDs	Gradient	~3	~23.9%	44	[90]
CdSeS QDs	Gradient	2.1 ± 0.6	30%	44	[91]

was kept at 180~200°C for 12 h and then air cooled to room temperature. The resultant precipitates were subsequently filtered and washed with absolute ethanol, dilute HCl solution, distilled water, and absolute ethanol in turn. Then the products were collected after being dried in vacuum at 70°C for 4 h. Both temperature and solvent have significant effects on the synthesis and incorporating process for solid solution CdSe<sub>1-x</sub>S<sub>x</sub> nanocrystallites. Higher temperature is needed for the formation of CdSe<sub>1-x</sub>S<sub>x</sub> nanowires and effective incorporating process of the solid solution when compared with those in the cases of CdS or CdSe, because lower temperature cannot provide enough activation energy to form the solid solution CdSe<sub>1-x</sub>S<sub>x</sub>, and the activation energy to form a solid solution increases as the S and Se content becomes equal. Ethylenediamine is a protophilic base solvent and bidentate ligand containing two N-chelating atoms, which plays a key role in the formation of CdSe<sub>1-x</sub>S<sub>x</sub> nanowires. When CdC<sub>2</sub>O<sub>4</sub> was added into ethylenediamine, a complex ion [Cd(en)<sub>n</sub>]<sup>2+</sup> formed in the solvothermal process. The formation mechanism of CdSe<sub>1-x</sub>S<sub>x</sub> nanowires may be related to the N-chelating effect of the bidentate ligand with Cd<sup>2+</sup> and the stronger hydrogen bonding action effect of the protophilic properties among ethylenediamine molecules. But the detailed formation mechanism of CdSe<sub>1-x</sub>S<sub>x</sub> nanowires has not been clear yet. Later, in 2006 [61], CdSe<sub>1-x</sub>S<sub>x</sub> nanorods were fabricated in ethylenediamine by a similar solvothermal process. In this case, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, CS(NH<sub>2</sub>)<sub>2</sub>, elemental Se, and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O as reactants were used. The reaction was carried out at 120~140°C for 10 h, and then reaction mixture was cooled to room temperature naturally. The resultant precipitates were washed with absolute ethanol and distilled water subsequently and then dried in air at 60°C for 4 h. The authors indicated that the formation process of the CdSe<sub>1-x</sub>S<sub>x</sub> nanorods could be divided into four steps: firstly, the reagents reacted to get amorphous CdSe<sub>1-x</sub>S<sub>x</sub> particles; secondly, the particles stripped into soft thin fibers; thirdly, these fibers sclerosed to needle-like fragments; and finally the needles grew to be highly crystallized. They also proposed that, unlike the formation process of ME (M = Zn, Cd; E = S, Se) nanorods in ethylenediamine, there was not an ethylenediamine intercalated precursor in that of CdSe<sub>1-x</sub>S<sub>x</sub> nanorods. Ethylenediamine as solvent was also crucial in the formation process of the rod-like morphology. And the reaction temperature decreased because a small amount of CdS nanorods formed in the process, which could

TABLE 4: The reaction conditions for CdSeS QDs synthesized by microwave irradiation.

System	Cd precursor	Se precursor	S precursor	Temperature (°C)	Time (min)	Refs.
CdSeS QDs	CdCl <sub>2</sub> + MPA	NaHSe	MPA	140	5–60	[41]
CdSeS QDs	CdCl <sub>2</sub> + MPA	Na <sub>2</sub> SeSO <sub>3</sub>	MPA	130	30	[90]
CdSeS QDs	CdCl <sub>2</sub> + MPA	Na <sub>2</sub> SeSO <sub>3</sub>	MPA	No data	No data	[91]

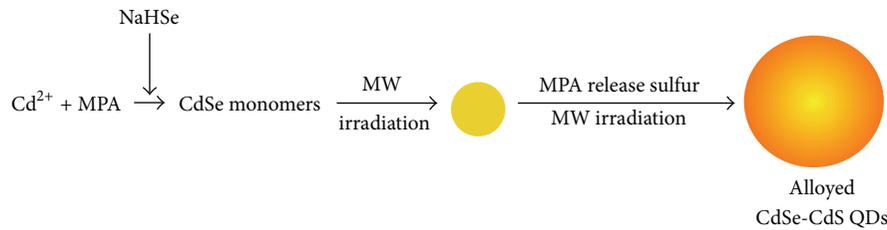


FIGURE 4: Schematic for the formation process of alloyed CdSeS QDs by microwave (MW) irradiation [41].

act as seeds for the crystallization of CdSe<sub>1-x</sub>S<sub>x</sub> crystals to reduce the formation energy of CdSe<sub>1-x</sub>S<sub>x</sub> products. In 2009 [94], employing the solvothermal synthesis route, CdSe<sub>1-x</sub>S<sub>x</sub> nanorods were also fabricated by using Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, S, and Se, respectively, as Cd, S, and Se source, ethylenediamine as solvent, and polyethylene glycol 2000 as the polymer-controller matrix and reacting at 180°C for 24 h. Before the source and solvent were put into the stainless steel autoclave, a PEG gel dosed with Cd<sup>2+</sup> needs to be made by adding Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O into polyethylene glycol 2000 gel and then stirring at room temperature for 5 h in order to achieve good dispersion of Cd<sup>2+</sup> in the polymer matrix. The formation of the CdSe<sub>1-x</sub>S<sub>x</sub> nanorods may follow a chemical solution transport growth mechanism [95]. During the synthesis, ethylenediamine was a strong bidentate solvent, readily chelating divalent cadmium ions. Therefore, an effectively reversible pathway as  $[\text{CdSe}]_n \xrightleftharpoons{\text{en}} n\text{Cd}^{2+} + n\text{S}^{2-} + n\text{Se}^{2-}$  might be established between the solution and solid phases, and this reversible pathway between the solution and solid phases played a key role in the crystal growth. Meanwhile, polyethylene glycol 2000 served as a molecular template in controlling the growth of CdS<sub>x</sub>Se<sub>1-x</sub> nanorods by connecting with the ethylenediamine to form chain structures with many pores. The possible growth model is shown in Figure 5. Due to the different processing parameters, the as-described 1D CdSeS nanowires or nanorods prepared by solvothermal synthesis method have different physical properties. For details, please check Table 5.

Solvothermal synthesis method is an efficient and facile method for preparing 1D CdSeS nanostructures. CdSSe nanowires or nanorods with high crystallinity and good orientation could be obtained by this method. However, there are some security issues within the process due to the volume expansion of the fluid in the sealed environment under heating treatment, which would create very high pressure. Hence, the compactedness of the autoclave should be cautious, which should not exceed 85% by volume (usually 80%). Moreover, the reaction process is unobservable because the reactions happened in a sealed reactor, and the reaction procedure is not monitored. So, it is difficult to

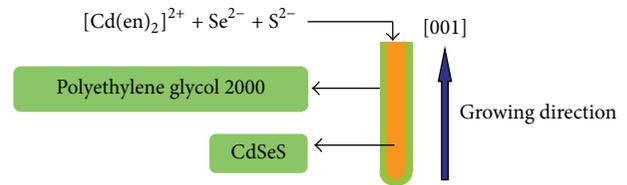


FIGURE 5: Possible growth model of CdSeS nanorods.

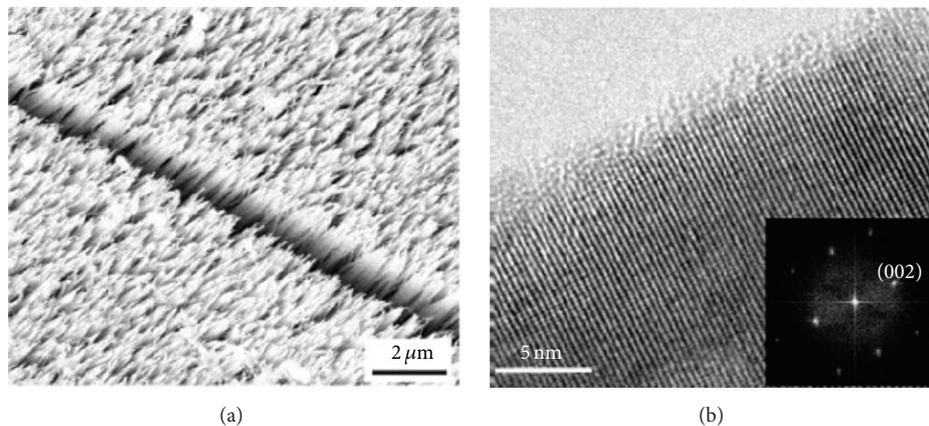
investigate the formation mechanism of CdSeS nanowires or nanorods.

**3.5. Template-Assisted Electrodeposition.** In 2005 [62], template-assisted electrodeposition was reported to prepare alloyed ternary CdSe<sub>1-x</sub>S<sub>x</sub> nanowires arrays, by which the ratio of S to Se in the nanowires could be controlled through adjusting the relative amounts of the starting materials. The detailed synthesis process is as follows: CdSe<sub>1-x</sub>S<sub>x</sub> nanowires were first galvanostatically electrodeposited into the pores of anodic aluminum oxide (AAO) membranes coated with a thin Au layer from a dimethyl sulfoxide solution containing CdCl<sub>2</sub>, elemental S, and elemental Se at 160°C for 15 min, and the deposition current density was kept constant at 2.4 mA/cm<sup>2</sup>. Then the nanowires embedded in the AAO template were annealed at 400°C under a N<sub>2</sub> atmosphere for 8 h. After that, the back Au layer of the nanowire/AAO/Au samples was removed by chemically dissolving them in 1.0 M NaCN aqueous solution. The resultant alloyed ternary CdSe<sub>1-x</sub>S<sub>x</sub> nanowires were highly crystalline (see Figure 6 [62]), and the band-gaps of these well-structured nanowires could be continuously tuned from 1.75 (CdSe) to 2.44 eV (CdS) through modulating the compositions of S and Se.

In the template-assisted electrodeposition process, the supplied electric field plays an important role in the synthesis of CdSe<sub>1-x</sub>S<sub>x</sub> nanowires. The higher potentials used in the ac deposition cycle (>5 V) could result in the codeposition of elemental Cd, and, for the ac process, the rate and direction of the diffusion would vary with the alternation of the electric field, thus resulting in a high density of defects and small

TABLE 5: Physical properties of 1D CdSeS nanostructures prepared by solvothermal synthesis.

CdSeS nanostructures	Diameter (nm)	Length ( $\mu\text{m}$ )	Crystal	Band-gaps (eV)	FWHM (nm)	Refs.
CdSeS nanowires	10–90	0.7–8	Hexagonal	No data	No data	[60]
CdSeS nanorods	10–20	100–150	Hexagonal	1.7–2.4	No data	[61]
CdSeS nanorods	15–20	100–200	Hexagonal	1.75–2.44	~25	[94]

FIGURE 6: (a) SEM image of the  $\text{CdSe}_{1-x}\text{S}_x$  nanowire arrays and (b) HRTEM image of an individual 20 nm  $\text{CdSe}_{1-x}\text{S}_x$  nanowire by template-assisted electrodeposition (insert in (b): the corresponding Fourier transformation of the entire HRTEM image) [62].

polycrystalline structure in the nanowires [96]. However, under dc deposition conditions, it is easy to control the potential as being no more than the codeposition potential of Cd, and the diffusing process is more likely to reach a steady state. Thus, the defects in the electrodeposited nanowires are largely decreased, and further alloyed ternary  $\text{CdSe}_{1-x}\text{S}_x$  nanowires with a high crystallinity could be obtained [62].

The template-assisted electrodeposition synthesis is a feasible approach to prepare highly crystalline  $\text{CdSe}_{1-x}\text{S}_x$  nanowires with continuous tunable band-gaps. It may open the possibilities of developing a variety of ternary or quaternary semiconductor nanowires based on II–IV and III–V materials. But, in such template-assisted electrodeposition synthesis, electric power supply is necessary, and it is an energy-wasting synthesis method.

**3.6. Thermal Evaporation.** Thermal evaporation is widely used to prepare CdSeS nanostructures via a vapor-liquid-solid (VLS) or vapor-solid (VS) process on a substrate coated with metal catalyst. It often comes true in a furnace at high temperature under inert gas flow. Typical process is shown in Figure 7.

In the thermal evaporation synthesis, the relative dominance between VLS and VS growth mechanisms determines the final shape of the nanostructures [97, 98]. At low substrate temperature under low vapor supply, the growth dominated by a VLS mechanism usually occurs and the resultant nanostructures usually have the form of nanowires. When both the vapor supply rate and substrate temperature increase, VS growth, which promotes side wall growth, starts to play a role, competing with the VLS mechanism. Those two combined growth mechanisms might result in tapered

nanobelts with catalysts on the tip [69]. In general, it requires more thermal energy to promote a VS growth than a VLS process [99]. Accordingly, more sample vapor and higher substrate temperature would enable a VS mechanism to play the governing role to grow nanobelts and nanosheets. In addition, the spontaneous polarization induced asymmetry (SPA) growth mechanism [100] could also happen in the growth of CdSeS nanostructures. In other words, self-catalyzed growth takes place predominantly on the chemically active, positively charged Cd side of the nanobelt, provided that sufficient thermal energy to surmount nucleation barrier is supplied, while the chemically inert, negatively charged Se/S side of the nanobelt is relatively flat [69]. Usually, the SPA growth mechanism results in toothed nanobelts or nanosaw structures. And this thermal evaporation synthesis often employs substrates coated with a thin gold film, and, during the growth, gold agglomeration takes place to form nanosized islands, which act as catalysts.

Another viewpoint has been proposed to explain the S suppression effect. It pointed out that the interplay between the VLS and VS mechanisms may play a role during the growth of CdSeS nanostructures [69]. In a traditional VLS model, supersaturated CdS/CdSe in molten gold droplets starts to precipitate at the interface between liquid and solid to form a nanowire. Solubility differences between S and Se species together with the relative vapor supply rates of both species will determine the molar fraction of CdSeS nanostructures. While a VS growth mechanism dominates, S and Se species initially arriving at the nanobelt top/bottom surfaces migrate toward the  $\pm(0001)$  side surfaces for incorporation. The competition between S and Se species occurs and a strong preference for the incorporation of Se species may exist.

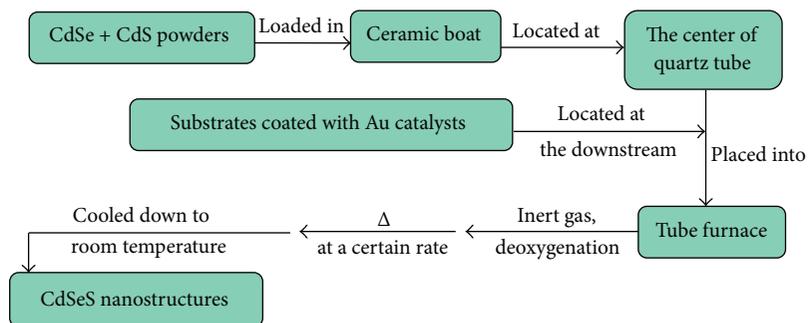


FIGURE 7: Typical process of thermal evaporation.

So, at high temperatures, CdSeS nanosheets with very small S incorporation would result even if a sufficient amount of S vapor is transported.

The thermal evaporation process of growing CdSeS nanostructures can be divided into one-step and two-step ones. In the one-step one, a CdSe and CdS mixture powder as the precursor was loaded into a ceramic boat and located at the center of quartz tube. Then by heating the precursor powder at an appropriate temperature, CdSeS nanostructures are formed onto the substrate under the gas flow downstream, while, in the two-step process, a CdSe powder was usually loaded into the ceramic boat alone in the quartz tube. And CdSe nanostructures were grown for a certain time firstly. Then after the temperature was decreased to a desired value while the flow of the forming gas was kept, the CdSe powder was replaced with CdS powder quickly to grow CdSeS nanostructures. The two-step process can overcome the difficulty in controlling S incorporation during the growth of large-area CdSeS nanosheets at high temperature [97].

In 2005 [8], Pan et al. reported the synthesis of single-crystal ternary CdSe<sub>1-x</sub>S<sub>x</sub> nanobelts with site-controlled compositions via one-step thermal evaporation process. The resultant CdSe<sub>1-x</sub>S<sub>x</sub> nanobelts have a strong single emission band near their band-edges, and these spectral peaks could be tuned from ~508 nm (for pure CdS) to ~705 nm (for pure CdSe). Using this one-step thermal evaporation synthesis, products covering the entire composition range ( $X$  varied from 1 to 0) could be typically obtained on a single substrate, but they were usually of less uniformity because the composition of the nanostructured CdSe<sub>1-x</sub>S<sub>x</sub> was highly dependent on the local substrate temperature [10]. To solve this problem, in 2011 [13], Lu et al. designed a special substrate holder and successfully synthesized CdSe<sub>1-x</sub>S<sub>x</sub> nanobelts with uniform chemical stoichiometry and accurately controlled compositions. The schematic of the alloyed nanobelts growth reactor using the special substrate holder is shown in Figure 8. With such holder, substrates could be slotted vertically so that the plane of the substrates would face the incoming flux of CdSe<sub>1-x</sub>S<sub>x</sub> vapor during the growth. The vertically positioned substrate could be maintained at a fixed temperature during the growth, so samples with highly uniform composition in a large area could be obtained.

Many CdSeS nanostructures with excellent properties could be prepared directly by one-step thermal evaporation

process under different reaction conditions. Typical results are shown in Table 6.

There are also some CdSeS nanostructures prepared by two-step thermal evaporation process. For example, CdS/CdSe lateral heterostructure nanobelts were synthesized by growing CdSe nanobelts at 900°C for 2 h firstly by thermal evaporation and then putting CdS source into furnace after the CdSe nanobelts samples were cooled down to room temperature, and the products were finally prepared at 700–850°C for 2 h via similar thermal evaporation process [104]. Ternary CdSe<sub>1-x</sub>S<sub>x</sub> single-crystal nanoribbons (NRs) with uniform and controllable compositions were prepared by two successive thermal evaporation steps involving (i) growing CdSe NRs at 850°C for 40 min and (ii) growing CdSe<sub>1-x</sub>S<sub>x</sub> NRs at 750°C by sulfurizing the as-synthesized CdSe NRs using a constant atmosphere of 10% H<sub>2</sub>S and 90% Ar of 200 Torr [54]. And symmetrical composition-graded CdSe<sub>1-x</sub>S<sub>x</sub> nanowires were also fabricated by two-step thermal evaporation via growing CdS nanowires at 830°C for 30 min firstly and then putting CdSe source into furnace to react with the CdS nanowires for 15–30 min [56]. In addition, CdSeS lateral heterostructure nanosheets [64] were fabricated by such two-step thermal evaporation process, too. In the first step of the growth, only CdS powder was thermally evaporated at 880°C for 1 h. Then CdSe source was loaded into the furnace while the temperature was gradually lowered to 840°C and held for 40 min to grow the CdSeS lateral heterostructure nanosheets.

Thermal evaporation is a very good and facile method to prepare CdSeS nanostructures. However, it is hard to obtain high uniformity and selectivity of stoichiometry on a single substrate through this approach. Although special substrate holders, which can hold substrate vertically, can be designed and applied, it is not suitable for large-scale production. So an easy and feasible way to synthesize 1D ternary nanostructure with uniform composition on a reasonably large substrate is desired.

**3.7. Pulsed Laser Deposition.** Pulsed laser deposition (PLD) synthesizes materials via vapor-phase transport process of a source vapor ablated by pulsed laser of a certain wavelength onto a substrate. It works in a hot-wall high-temperature PLD system as shown in Figure 9 [9]. It can be used to synthesize 1D CdSeS nanowires. The main procedure of PLD synthesis

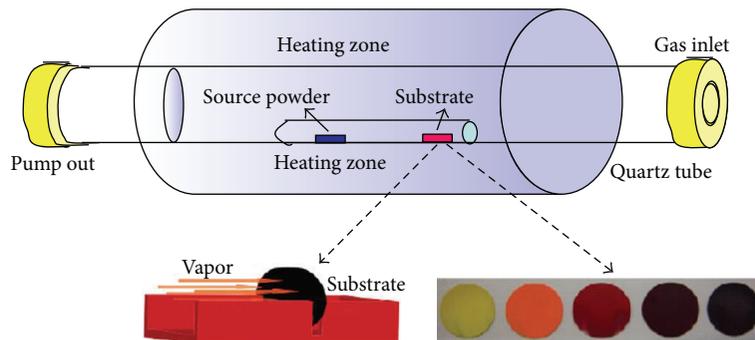


FIGURE 8: Schematic of alloyed nanobelts growth reactor using the special substrate holder [13].

TABLE 6: The reaction conditions for CdSeS nanostructures prepared by one-step thermal evaporation.

CdSeS nanostructures	Evaporation sources	Substrate	Catalyst layer	Protection gas	Temperature (°C)	Time (min)	Refs.
CdSe <sub>1-x</sub> S <sub>x</sub> nanobelts	CdS, CdSe	Silicon slices	Au, ~2 nm	He	900	60	[8]
CdSeS whiskers	CdS, CdSe	Silicon slices	Au, 10 nm	He	850	120	[20]
Si-CdSeS core-shell nanowires	CdS, CdSe, silicon wafer	Quartz substrate	Au, 6 nm	Ar	1080	60	[75]
CdSe <sub>1-x</sub> S <sub>x</sub> nanobelts	CdS, CdSe	Si substrate	Au	He	900	No data	[50]
CdSeS nanosheets	CdS, CdSe	Si substrate	Au, 5–10 nm	N <sub>2</sub> + 10% H <sub>2</sub>	850–900	60	[69]
CdSeS nanowires	CdS, CdSe	Si wafers	Au, 2 nm	N <sub>2</sub>	(1) 830 (2) 800	(1) 40 (2) 60	[101]
CdSe <sub>1-x</sub> S <sub>x</sub> nanobelts	CdS, CdSe	Sapphire wafer	Au, ~1 nm	He	850	30	[13]
CdSeS nanowire arrays	CdS, CdSe	Mica substrate	Poly-l-lysine, 5 nm	Ar + 5% H <sub>2</sub>	750	30	[102]
CdSe <sub>1-x</sub> S <sub>x</sub> nanobelts	CdS, CdSe	C-plane sapphire	Au	He	850	30	[103]
CdSeS nanowires	CdS, CdSe	Silicon wafer	Au, 30 nm	He	900	60	[44]

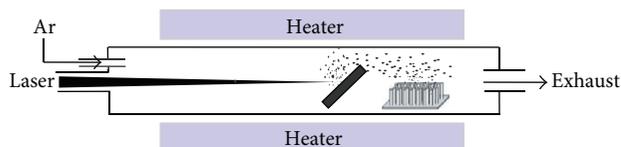


FIGURE 9: Schematic of a hot-wall high-temperature PLD system [9].

method to prepare CdSeS nanowires is shown as follows: (1) CdSeS compacts as targets were prepared by sintering pure CdS and CdSe powders at high temperature. (2) The as-prepared targets were ablated by an excimer laser, which were placed at the center of the reaction chamber, while the substrate coated with a thin Au layer (typically with a thickness of 5–30 Å) was located in the region where the temperature was sustained in a proper range and for a desired duration of time. The pressure in the processing tube was controlled within the range of 1–10 Torr.

In the synthesis, Au was used as catalyst, and the deposited Au layer contributed to the formation of Au-CdSe<sub>1-x</sub>S<sub>x</sub> eutectic alloying liquid when the reaction temperature is above the eutectic temperature. The liquid-phase

alloy enables the rapid growth of CdSe<sub>1-x</sub>S<sub>x</sub> nanostructure at a relatively low temperature. Laser ablation generates catalytic clusters with nanometer diameter that define the size and direct the growth of crystalline CdSeS nanowires by vapour-liquid-solid (VLS) mechanism in the synthesis process.

Several kinds of CdSeS nanowires were successfully prepared by different groups via PLD synthesis method. Their synthesis conditions of CdSeS nanowires were summarized in Table 7, and the physical properties of the corresponding prepared CdSeS nanowires are listed in Table 8.

PLD synthesis is an easy handling method to prepare CdSeS nanowires. But it is of high cost and has difficulty controlling the conditions to obtain CdSeS nanostructures with uniform size distribution and controllable structures.

#### 4. Conclusions and Outlook

CdSeS alloy nanostructures have attracted more and more attention due to their diversity of electronic and optical properties, presenting great potential for the applications in tunable optoelectronic devices and biomedical sciences. Many CdSeS nanostructures with different morphologies and properties were prepared to meet the needs of applications

TABLE 7: The synthesis conditions of CdSeS nanowires in PLD synthesis.

System	Thickness of Au layer (Å)	Target sintering temperature (°C)	Laser wavelength (nm)	Laser energy density ( $\text{J}\cdot\text{cm}^{-2}$ )	Deposition temperature (°C)	Refs.
$\text{CdS}_x\text{Se}_{1-x}$ nanowires	5–30	700	248	1–5	400–1100	[54]
$\text{CdS}_x\text{Se}_{1-x}$ nanowires	5–30	1000	248	1–5	400–1100	[9]
$\text{CdS}_x\text{Se}_{1-x}$ nanowires	5–30	1000	248	1–5	550	[56]

TABLE 8: Typical properties of  $\text{CdS}_x\text{Se}_{1-x}$  nanowires prepared by PLD.

System	Diameter (nm)	Length ( $\mu\text{m}$ )	Crystal structure	Band-gap (eV)	Refs.
$\text{CdS}_x\text{Se}_{1-x}$ nanowires	70–100	~10	Wurtzite	1.75–2.45	[54]
$\text{CdS}_x\text{Se}_{1-x}$ nanowires	50–100	10–50	Wurtzite	1.74–2.45	[9]
$\text{CdS}_x\text{Se}_{1-x}$ nanowires	100–200	Dozens	Wurtzite	1.73–2.43	[56]

by different synthesis methods. And, these synthesis methods have different advantages and disadvantages. Hot-injection synthesis is a good method to prepare CdSeS nanocrystals or quantum dots with high tunable luminescence properties and narrow size distribution, but it involves toxic organic solvents and performs poorly in synthesis reproducibility; so finding replaceable green solvents and improving the reproducibility of this method are needed. One-pot, noninjection synthesis is suitable for large-scale production of CdSeS nanostructures; however, how to enhance quantum yield of CdSeS nanostructures is still a problem. The thermal and nonthermal effects of microwave irradiation synthesis have been still poorly understood, which limits its application. Solvothermal synthesis can prepare 1D CdSeS nanostructures with high crystallinity and good orientation, but the reaction should be carried out in a sealed reactor, in which the procedure cannot be monitored in time; so the growth mechanism of CdSeS nanostructures by this method is difficult to study. Template-assisted electrodeposition synthesis is a high cost and energy-wasting method, due to the fact that it needs continuous electric power supply during the synthesis process. Thermal evaporation synthesis is an easy handling method to prepare CdSeS nanostructures; at present, the challenge for it is how to obtain CdSeS nanostructures with high uniformity for the large-scale production. And pulsed laser deposition synthesis has difficulty controlling the experimental conditions to prepare CdSeS nanostructures with controllable structures. Consequently, though so many synthesis methods were proposed to prepare CdSeS nanostructures and many attempts have been tried to improve these methods, methods which are safe, economic, environment-friendly, and suitable for large-scale production of alloyed CdSeS nanostructures with high photoluminescence, high stability, and low/no cytotoxicity are still much desired.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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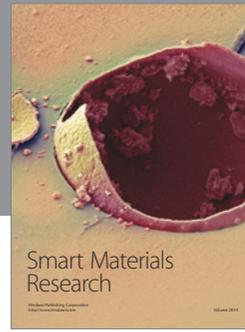
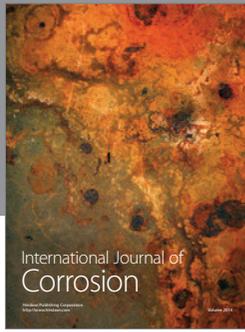
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