Zn$_x$Cd$_{1-x}$Se nanomultipods with tunable band gaps: synthesis and first-principles calculations

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**Zn\textsubscript{x}Cd\textsubscript{1−x}Se nanomultipods with tunable band gaps: synthesis and first-principles calculations**

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**Abstract**

In this paper, we demonstrate that Zn\textsubscript{x}Cd\textsubscript{1−x}Se nanomultipods can be synthesized via a facile and nontoxic solution-based method. Interesting aspects of composition, morphology and optical properties were deeply explored. The value of Zn/(Zn + Cd) could be altered across the entire range from 0.08 to 0.86 by varying the ratio of cation precursor contents. The band gap energy could be linearly tuned from 1.88 to 2.48 eV with respect to the value of Zn/(Zn + Cd). The experiment also showed that oleylamine played a dominant role in the formation of multipod structure. A possible growth mechanism was further suggested. First-principles calculations of band gap energy and density of states in the Vienna \textit{ab initio} simulation package code were performed to verify the experimental variation tendency of the band gap. Computational results indicated that dissimilarities of electronic band structures and orbital constitutions determined the tunable band gap of the as-synthesized nanomultipod, which might be promising for versatile applications in relevant areas of solar cells, biomedicine, sensors, catalysts and so on.

(Some figures may appear in colour only in the online journal)

**1. Introduction**

Due to their excellent structural and electronic properties, nanostructured materials based on II–VI group semiconductors have been recognized as one of the most important groups of materials for optoelectronic and biomedical devices in recent years [1–4]. Apart from the unique properties of nanostructured materials, the control of their nanostructures has also received a great deal of attention, and hence has contributed to the development of nano-based devices [5]. For example, Gradecak \textit{et al} found that, in contrast to nanoparticles, high-aspect-ratio nanowires could enhance electron transport and improve the performance of photovoltaic devices, because their direct electron transfer pathways are independent of electron hopping [6]. In this situation, II–VI group nanomaterials with simple structures such as quantum dots or nanorods [7, 8], as well as those with more complicated structures such as nanorings, nanobreaches or nanomultipods, have been reported and investigated [9–11].

According to earlier research, the nanomultipod has become a hot topic in view of its unique properties, such as larger surface area than traditional 1D nanostructures [12]. The subsequent study of multipod nanostructures would effectively promote their availability [13]. Up to now, some II–VI group nanomaterials with multipod structures have been reported, including ZnSe, CdS and CdSe [14–16]. Both ZnSe
and CdSe have been reported to have significant applications in certain fields [17–20]. The emission wavelengths of ZnSe and CdSe lie in the near-ultraviolet and near-infrared regions respectively, so their applications are restricted by the limited range of the band gap. As we know, band gap engineering could effectively improve the performance of nanoscopic semiconductor devices [21]. By combining ZnSe and CdSe together in different ratios, fluorescent light throughout the whole visible spectrum could be emitted, exhibiting versatile utilities in several areas [21]. Therefore, it is essential for nanocrystal-based devices to have tunable band gaps [22].

To the best of our knowledge, the synthesis of ZnCdSe nanomultipods has not been reported previously. Besides, in the widely used method to synthesize selenide nanocrystals, trioctylphosphine (TOP) serves as the solvent for Se powder and the injection of TOP–Se precursor is necessary [7, 23]. Since TOP is poisonous, unstable and expensive, it is necessary to find a nontoxic and less expensive substitute for large-scale production.

Herein, we present a facile, solution-based one-pot method for synthesis of ZnCdSe nanomultipods. Compared with the traditional hot-injection method, this method is more convenient for large-scale production. Characterizations of compositions, structures and morphologies have also been performed in our work. Experimental measurements indicated that the band gap energy (Eg) of the ZnCdSe nanomultipods could be linearly tuned with the variation in composition. Moreover, we found that the solvent played an important role in determining the ultimate shape of the products. Considering different physical and chemical properties of solvents, we also put forward a nucleation-induced, surfactant-assisted mechanism to explain the formation of the nanomultipods.

Meanwhile, with the assistance of theoretical investigation, it would be possible for us to carry out effective band gap engineering and thus to manipulate the properties of nanomaterials easily in future applications. However, investigation of ZnCdSe in this area almost remains void. In this case, we further reported first-principles calculations of the density of states (DOS) and Eg of ZnCdSe in the Vienna ab initio simulation package (VASP) code [24–27], in order to make our work theoretically feasible. The theoretical analysis demonstrated the validity of the experimentally obtained variation tendency of bandgap versus composition. The Eg was verified to be tuned by varying the ratio of Zn/Cd. All of the above indicates that ZnCdSe nanomultipods would be promising for future applications in photovoltaic and biomedical devices.

2. Experimental details

2.1. Synthesis of ZnCdSe nanomultipods

Zinc acetylacetonate (Zn (acac)₂, >97.0%), cadmium acetylacetonate (Cd (acac)₂, >98.0%), selenium (Se, >99.95%), oleylamine (OM, 90%) and oleic acid (OA, 90%) were purchased from Aladdin, without further purification. In a typical synthesis of ZnCdSe nanomultipods, a 2 mmol mixture of Zn (acac)₂ and Cd (acac)₂, 2 mmol Se and 30 ml OM were added into a two-necked flask (100 ml) at room temperature. The mixture was heated to 110 °C and kept for 30 min after vacuum pumping and N₂ bubbling. Then the solution was heated to 250 °C and kept for 4 h with vigorous stirring under N₂ atmosphere. After the solution was naturally cooled to room temperature, the product was purified by a standard polar/nonpolar solvent precipitation technique. Finally, the product was dissolved and kept in chloroform.

2.2. Characterization methods

An Oxford INCA energy-dispersive x-ray spectroscopy (EDS) detector was employed to analyze the elemental compositions. The crystal structure of ZnCdSe nanomultipods was characterized by powder x-ray diffraction (XRD) using Cu Kα radiation (λ = 1.54 Å). Transmission electron microscope (TEM) images were taken by a JEM 2100 microscope at an accelerating voltage of 200 kV. To prepare TEM specimens, several drops of chloroform solution were deposited onto a carbon-coated copper grid and then evaporated in the open air. UV–vis absorption spectra of ZnCdSe nanomultipods were measured by a Lambda 20 UV–vis spectrometer.

2.3. Theoretical calculation details

Local density approximation (LDA) calculations were performed using the plane-wave code VASP. The frozen core projector-augmented-wave (PAW) method was used to represent the interactions between electrons and atomic nuclei, since it was more accurate than the ultrasoft pseudopotentials. In the program, a plane-wave basis set was adopted to provide good access to the Hellmann–Feynman forces acting on all the atoms in the supercell. A plane-wave cutoff energy corresponding to a kinetic energy of 300 eV was employed. The Brillouin zone (BZ) of ZnCdSe is sampled using a 4 × 4 × 1 Monkhorst–Pack k grid.

3. Results and discussion

The chemical compositions of six ZnCdSe samples detected by EDS are displayed in table 1. From the EDS data, the stoichiometries of the six samples, named as sample I, II, III, IV, V and VI, are Zn₀.08Cd₀.92Se, Zn₀.16Cd₀.84Se, Zn₀.29Cd₀.71Se, Zn₀.44Cd₀.56Se, Zn₀.68Cd₀.32Se and Zn₀.86Cd₀.14Se, respectively. Moreover, the relationship between compositions of the six samples and the Zn ratio (Zn/(Zn + Cd), x) of the precursors is shown in figure 1. A nearly linear relationship suggests that the Zn precursor and Cd precursor have similar reactivities in this experiment.

Figure 2(a) exhibits the XRD patterns of six samples as well as the standard patterns of ZnSe (JCPDS, No 15-0105) and CdSe (JCPDS, No 77-2307). The experimental patterns agree well with the standard ones for wurtzite structure, with four main peaks, (002), (110), (103) and (112). In figure 2(c), it is found that the strongest peak (002) moves from 25.67° (x = 0.08) to 27.10° (x = 0.86) as the ratio of Zn/(Zn + Cd) increases. Such a systematic shift of diffraction
TEM observation by Ding et al. the process of nucleation, not all nuclei could successfully formation of tetrapod structure [30, 31]. However, during ⟨001⟩ orientation and thus lead to the formation of tetrapod structure [30, 31]. However, during the process of nucleation, not all nuclei could successfully grow along the ⟨001⟩ orientation (the fast growth fronts) took place. Different morphologies such as bipod and tetrapod were formed, depending on the number of fast growth fronts. If we use oleic acid instead of oleylamine, the whole ZnCdSe core including those fast growth fronts might be capped and stop growing, because oleic acid is a stronger coordinating ligand than oleylamine [35, 36]. Consequently, ZnCdSe nanoparticles would appear. This investigation is preliminary, and the mechanism still needs further exploration.

peaks is due to the contraction of lattice parameters when Zn atoms replace Cd sites in the ZnCdSe lattice. It can be inferred that, as the ratio of Zn/(Zn + Cd) rises, a decreasing tendency of interplanar spacing appears because of the crystal contraction. Moreover, derived by extrapolating a straight line to cross the vertical axis (figure 2(b)), the interplanar spacings of the (002) plane are around 0.3491 (CdSe) and 0.3258 nm (ZnSe), which are close to the ideal values in the standard PDF cards (0.3505 nm for CdSe and 0.3250 nm for ZnSe). The XRD data confirm the homogeneous nature of the crystals. Estimated from the full width at half maximum (FWHM) of the strongest (002) peaks by the Scherrer equation, the domain size of the ZnCdSe nanomultipods are around 3 nm. Figure 2(d) displays the wurtzite structure of Zn0.5Cd0.5Se from three different views. Sarasamak et al. once reported that for CdSe, at ambient conditions, the wurtzite structure is more stable with a lower energy level [28], which might explain why ZnCdSe shares the same structure.

Figure 3(a) shows TEM images of the as-synthesized ZnCdSe nanomultipods (sample VI, x = 0.86). The statistic average diameter of all the nanomultipods, which is exhibited in figure 3(c), is around 3–3.5 nm, only having a slight error compared with the result calculated by the Scherrer equation. The high resolution TEM images (figure 3(b)) present well resolved lattice fringes of the (002) plane of a ZnCdSe bipod with interplanar spacings of 0.3301 nm and 0.3279 nm respectively in two different legs, and the values fit well with the results calculated from XRD data (0.3288 nm).

Clearly, the nanostructures in figure 3(a) have mixed morphologies, including bipod, tripod and tetrapod. To explain the shape diversity of the products, we should pay attention to the fundamental mechanism. Alivisatos et al. showed the seeded growth of a CdSe/CdS nanotetrapod, which was composed of two main parts: nucleation and growth [29]. Although a different synthesis method was employed, nucleation and growth should still be important in the formation of the nanomultipods.

The first part is the nucleation. According to the TEM observation by Ding et al., the ideal shape of the nanomultipod’s crystal core is an octahedron [30]. The four cation-terminated positively charged planes could serve as fast growth fronts for the crystal with wurtzite structure to grow along the ⟨001⟩ orientation and thus lead to the formation of tetrapod structure [30, 31]. However, during the process of nucleation, not all nuclei could successfully evolve into perfect octahedrons. As for CdS and CdSe, it is widely accepted that heterogeneous nucleation, which might happen on the phase boundaries or other preferential sites, occurs much more readily than homogeneous nucleation, because its energy barrier is lower [32, 33]. Moreover, homogeneous and heterogeneous nucleation could take place synchronously during the reaction, but thermodynamically there should be more heterogeneous-formed nuclei than homogeneous-formed ones. Homogeneous-formed nuclei surrounded by a liquid medium might grow into octahedrons eventually, while heterogeneous-formed ones might only have two or three fast growth fronts. As a result, the other morphologies such as bipod or tripod would appear in the final products, accounting for a large proportion. Figure 3(a) shows that the number of tetrapods was much lower than the number of bipods or tripods, which corresponds well with our prediction.

Figure 1. The relative composition amount of product versus precursor of ZnCdSe nanomultipod (inset: the EDS spectrum of sample VI).

Table 1. Chemical compositions of ZnCdSe nanomultipod determined from EDS analysis. The data collected by EDS should be considered to have ±2% uncertainty in the elemental composition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn/(Zn + Cd)</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.08</td>
<td>Zn 3.8 Cd 45.0 Se 51.2</td>
</tr>
<tr>
<td>II</td>
<td>0.16</td>
<td>Zn 6.6 Cd 34.2 Se 59.2</td>
</tr>
<tr>
<td>III</td>
<td>0.29</td>
<td>Zn 13.3 Cd 32.8 Se 53.9</td>
</tr>
<tr>
<td>IV</td>
<td>0.44</td>
<td>Zn 18.8 Cd 23.9 Se 57.3</td>
</tr>
<tr>
<td>V</td>
<td>0.65</td>
<td>Zn 28.1 Cd 15.5 Se 55.4</td>
</tr>
<tr>
<td>VI</td>
<td>0.86</td>
<td>Zn 42.2 Cd 6.8 Se 51.0</td>
</tr>
</tbody>
</table>
Figure 2. (a) XRD patterns of six samples (ZnSe, JCPDS No 15-0105, dark yellow; CdSe, JCPDS No 77-2307, yellow); (b) interplanar spacing of ZnCdSe nanomultipod with increase of Zn ratio; (c) shift of (002) peak with increase of Zn ratio; (d) wurtzite crystal structure of ZnCdSe nanomultipod.

Figure 3. (a) TEM image of sample VI; (b) HRTEM image of sample VI; (c) Diameter distribution of sample VI.

In addition, figure 4 provides the basic information of ZnCdSe nanoparticles. Observed from both TEM and HRTEM images (figures 4(b) and (c)), ZnCdSe nanoparticles have an average diameter of around 20 nm. EDS data (figure 4(a)) show that the composition of this sample is Zn$_{0.85}$Cd$_{0.15}$Se, quite close to the composition of sample VI. Estimated from the UV–vis absorption spectrum, the band gap of the as-synthesized ZnCdSe nanoparticles is about 2.25 eV (figure 4(d)), which is a little smaller than the band gap of sample VI (2.48 eV, figure 5(a)) owing to the larger confinement size.

Figure 5(a) displays the UV–vis absorption spectra of six samples with a similar diameter of around 3.5 nm. The optical data are estimated at the near-absorption edge using
Figure 4. (a) EDS spectrum, (b) TEM image, (c) HRTEM image, and (d) UV–vis absorption spectrum of ZnCdSe nanoparticles (inset: obtained band gap energy of ZnCdSe nanoparticles).

To gain more insight into theoretical study, first-principles calculations were utilized to obtain the band gap versus the ratio of \( Zn/(Zn + Cd) \). Figure 6(a) shows the theoretical band structure of ZnCdSe \((x = 0.9375)\) calculated with the generalized gradient approximation (GGA) function. The band gap values of ZnCdSe calculated through the GGA functional method are shown in figure 6(b). We selected six typical samples of ZnCdSe, with the \( x \) values of 0.125, 0.25, 0.375, 0.5625, 0.75 and 0.875. As regards the variation tendency of \( E_g \), the result of theoretical calculations is consistent with the result of experimental investigations. The values of \( E_g \) display a linear upward tendency with the increase of \( x \). The \( E_g \) is 1.0741 eV when \( x \) is 0.125, while the value is 1.2675 eV when \( x \) equals 0.9375. For the variation of \( E_g \) obtained from computational results, an appropriate explanation might be that the Cd replacement by Zn influences the distribution of electronic structure in the whole crystals.

to further investigate the reasons, we also calculated the DOS of ZnCdSe with different \( Zn/(Zn + Cd) \) ratios as exhibited in figure 7 when the energy zero was taken at the Fermi energy level (EF). Therefore, we could analyze the electronic structures of ZnCdSe nanomultipoles and their potential influence factors. A comparison was made among the three DOS curves including \( Zn_{0.375}Cd_{0.625}Se \), \( Zn_{0.5625}Cd_{0.4375}Se \) and \( Zn_{0.75}Cd_{0.25}Se \). In general, the three DOS curves share a similar shape except for a few minute differences. Observed from some parts, it could be noticed that the shapes of the DOS curves actually take on

The dependence of \( E_g \) on the ratio of \( Zn/(Zn + Cd) \) could be described by the extended Vegard’s law [42, 43]:

\[
E_{ZnCdSe}^{-g}(x) = E_{ZnSe}^{-g} + (1 - x)E_{CdSe}^{-g} - bx(1 - x)
\]

where \( b \) refers to the specific ‘optical bowing constant’, which determines the degree of nonlinearity. However, in the case of ZnCdSe nanomultipoles, the parameter \( b \) is small enough to be considered zero. The atom size, electronegativity values of ions, and lattice constants of the binary structures (ZnSe and CdSe) should be taken into account for the phenomenon of less nonlinearity. Therefore, the mere 7% lattice mismatch between ZnSe and CdSe might be an explanation of the linearity exhibited in the fitted curve in the inset of figure 5(a).

The formula [37, 38]

\[
\alpha = K \frac{(h\nu - E_g)^{n/2}}{h\nu}
\]

where \( h\nu \) is the photon energy, and \( K \) and \( n \) are parameters. For the indirect band gap, the value of \( n \) is equal to 1, while it is equal to 4 for the direct band gap. The optical band gaps are calculated by extrapolating straight lines of the plots \((ah\nu)^2\) versus \( h\nu \) [39, 40] (figures 5(b) and (c)). This reveals that the band gaps of the six samples range from 1.88 \((x = 0.08)\) to 2.48 eV \((x = 0.86)\), which indicates the increasing tendency of a tunable band gap in ZnCdSe nanomultipoles with the increase of Zn/(Zn + Cd) ratio (inset of figure 5(a)). Such a tendency might be explained by the narrower band gap of CdSe (bulk: 1.74 eV) compared with that of ZnSe (bulk: 2.62 eV) [41].

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different tendencies in the regions near the valence band and conduction band. The states near the valence band maximum (VBM) are mainly derived from Zn-p, Cd-p and Se-p orbitals, and the states near the conduction band minimum (CBM) are composed of Zn-s, Cd-s and Se-p orbitals. Compared with the CBM, the influence of Zn and Cd is more obvious in the valence band. It is the different constitutions and significant contribution orbitals in VBM and CBM that cause the dissimilarities between them.

4. Conclusions

In summary, a facile synthetic strategy for cation-alloyed ZnCdSe nanomultipods was described for the first time. The composition could be tuned across the entire $x = 0.08$–0.86 range. The interplanar spacing decreased with respect to the increase of $x$, while the band gap energy of ZnCdSe could be tuned from 1.88 to 2.48 eV by increasing the content of Zn, fitting consistently with Vegard’s law. Such a linear variation tendency of band gap energy was verified by further theoretical calculations in the VASP code. Moreover, a possible formation mechanism was proposed based on the role of solvents. The advantageous structural and optical properties demonstrated that a composition-tunable cation-alloyed II–VI group nanomultipod would be a promising candidate for versatile applications in relevant areas of solar cells, biomedicine, sensors, catalysts and so on.

Acknowledgments

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