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Abstract: Distinct from the popular opinion that the only zincblende CuInS$_2$ phase could be prepared at the presence of oleic acid (OA), CuInS$_2$ nanocrystals with different phase structures and shapes were synthesized by a facile heat-up method through simply adjusting the OA dosage. Zincblende CuInS$_2$ quantum dots (QDs) with a triangular pyramid shape were obtained at a low dosage of OA (< 1 mL). With an increase in the OA dosage (~1.5 mL), wurtzite CuInS$_2$ hexagonal nanoplates were formed accompanying with zincblende CuInS$_2$ QDs. A higher OA dosage (2~3 mL) led to the production of wurtzite CuInS$_2$ hexagonal nanoplates. The formation of the CuInS$_2$ nanocrystals with tunable structures was mainly attributed to the role of OA dosage in the formation and transformation of a CuIn(SR)$_x$ intermediate. A high OA dosage could facilitate the formation and crystallization of the intermediate, giving a metastable wurtzite CuInS$_2$ structure which can be gradually converted into stable zincblende CuInS$_2$ QDs as the reaction proceeded. But a low OA dosage would lead to a low crystallinity of the intermediate, and thus transformation into zincblende CuInS$_2$ phase easily. Therefore, our work could provide guidance for the controllable synthesis of other multi-component chalcogenide nanocrystals.

Introduction

At present, colloidal semiconductor nanocrystals have attracted much scientific attention due to their size and shape dependent properties and applications in the various fields.\cite{1-3} As a typical ternary chalcogenide material, CuInS$_2$ is a I-III-VI$_2$ direct semiconductor with a bulk band gap of 1.45 eV, high extinction coefficient in the visible spectral range, exceptional radiation hardness and low toxicity.\cite{4-6} Therefore, CuInS$_2$ has been the focus of much recent research, and are widely used as light-emitting and solar-harvesting materials.\cite{7-9} CuInS$_2$ has three crystal structures: chalcopyrite, zincblende and wurtzite.\cite{10,11} Chalcopyrite CuInS$_2$ is thermodynamically favored at room temperature whereas the zincblende and wurtzite structures are stable only at high temperatures. In the zincblende and wurtzite structures, the indium and copper atoms are randomly distributed over the cation sites of the lattice\cite{12,13} which allows a flexibility of stoichiometry and thus tunes the Fermi energy over a wide range. Due to the difference in the three structures, CuInS$_2$ nanocrystals will exhibit different optical properties by controlling their phase structure.

Recently, the most common synthesis methods of CuInS$_2$ nanocrystals include solvothermal method,\cite{14,15} hot-injection method\cite{16,17} and heat-up method.\cite{18,19} Pan et al. first reported CuInS$_2$ nanocrystals with the zincblende and wurtzite structure by using dodecanethiol and OA as capping agent, respectively.\cite{20} In particular, Liu et al. found that CuInS$_2$ nanoplates with wurtzite-zincblende polytypism could be synthesized by one-pot thermolysis of a mixture solution of metal chlorides, 1-dodecanethiol and OA in 1-octadecene.\cite{21} They also prepared zincblende nanoparticles and wurtzite nanoplates by simply altering the dosage of 1-dodecanethiol. In the above reports, OA is usually used as a surfactant to avoid the aggregation of nanocrystals\cite{21,22} or as a capping agent to synthesize CuInS$_2$ nanocrystals with a certain phase.\cite{23,20,24} As is known, OA can affect the decomposition rate of metal precursors\cite{25,26} and thus put important effects on the nucleation rate of CuInS$_2$ nanocrystals which can determine the phase of nuclei.\cite{10} In this sense, the phase structure of CuInS$_2$ nanocrystals will be affected by OA dosage. However, there have been no reports so far that the phase structure of CuInS$_2$ nanocrystals can be tuned by varying the OA dosage. This is probably because the phase selectivity mechanism of CuInS$_2$ nanocrystals is still unclear. Therefore, it is of great significance to investigate the phase selectivity mechanism in detail.

Herein, CuInS$_2$ nanocrystals with tunable structures were synthesized by a facile heat-up method through altering the OA dosage. Zincblende QDs with a triangular pyramid shape were synthesized at a low OA dosage (< 1 mL) while a mixture of zincblende CuInS$_2$ QDs and wurtzite CuInS$_2$ nanoplates were formed at a moderate OA dosage (~1.5 mL). When a high OA
dosage (2–3 mL) was used, wurtzite nanoplates were obtained but a few wurtzite nanoplates would be dissolved to form zincblende QDs as the reaction continued. Moreover, an OA assisted formation mechanism was proposed and discussed in detail for the production of CuInS2 nanocrystals with tunable structures. Finally, the optical properties of as-prepared CuInS2 nanocrystals were also investigated.

Experimental

Materials

All chemicals were used as received without further purification. Copper (I) chloride (CuCl, > 97.0%), indium (III) chloride tetrahydrate (InCl3·4H2O, 99.99%), 1-dodecanethiol (DDT), oleic acid (OA), n-hexane, toluene, acetone were purchased from Sinopharm Chemical Reagent Co., Ltd and 1-octadecene (ODE, 90%) was purchased from Aladdin.

Synthesis of CuInS2 nanocrystals

In a typical synthesis, 0.8 mmol CuCl, 0.8 mmol InCl3·4H2O, 2 mL DDT, x mL OA (x = 0, 1, 1.5, 2, 3) and (10-x) mL ODE were added to a 50 mL three-necked flask. The reaction mixture was degassed at 100 °C for 30 min. After that, the solution was heated to 200 °C under argon flow and kept there for 30 min. The obtained solution was cooled down to room temperature and precipitated by acetone, then isolated by centrifugation and the supernatant liquid was decanted. And, the isolated solid was dispersed in hexane. The above centrifugation and isolation procedure was repeated several times for purification of the prepared CuInS2 NCs. Finally, the products were redispersed in toluene or dried in the air at 80 °C under vacuum for further analyses.

Characterizations

The powder X-ray diffraction (XRD) measurements were performed using a D8 Advance X’Pert Pro X-ray diffractometer. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) images were taken with a JEM 2100F microscope operated at 200 kV. Selected area electron diffraction (SAED) patterns and energy dispersive X-ray spectra (EDX) were performed on the same microscope. X-ray photoelectron spectra (XPS) were recorded on an AXIS-Ultra DLD-600W X-ray photoelectron spectrometer. Fourier transform infrared spectra (FT-IR) were recorded on a Lambda 750S spectrometer. The as-prepared CuInS2 nanocrystals were dispersed in hexane and the optical absorption spectra were measured using a Shimadzu UV-1601 UV-vis spectrometer with pure toluene as the reference. At first, the pure hexane was added into a cuvette to take a baseline, and then the CuInS2 nanocrystals were dispersed in hexane into the cuvette for the UV-vis adsorption spectra.

Results and discussion

Synthesis and characterization of CuInS2 nanocrystals

CuInS2 (CIS) nanocrystals (NCs) were prepared by a heat-up method from 0.8 mmol CuCl, 0.8 mmol InCl3·4H2O and 2 mL DDT in noncoordinating solvent ODE with different dosages of OA. The XRD patterns of typical products synthesized using different OA dosages are shown in Fig. 1. The products prepared using low OA dosages (0 mL and 1 mL) are zincblende CIS while a wurtzite phase is obtained using higher OA dosages (2 mL and 3 mL). Moreover, a mixture of wurtzite and zincblende CIS is synthesized when the volume of OA is 1.5 mL. The difference between chalcopyrite phase and zincblende phase is very small, but the CIS NCs with zincblende phase usually have a diffraction peak of (200).20,26 And the absence of the (101), (103) and (211) reflection peaks of chalcopyrite structure can be an evidence for the zincblende structure.21,24 Compared with the simulated diffraction patterns,21,27 all the peaks marked in the XRD patterns of CIS nanocrystals match well. The typical TEM, HRTEM and SAED images of CIS nanocrystals obtained with different OA dosages are shown in Fig. 2. Triangular pyramid nanoparticles are observed in the samples synthesized using 1 mL OA (Fig. 2a) and the size of these triangular pyramids is around 6 nm, which is twice smaller than the exciton radius of CIS (4.1 nm).25 Thus, the zincblende nanocrystals with a triangular pyramid shape can be called as QDs. Both triangular pyramids QDs and hexagonal nanopolymers synthesized using 1.5 mL OA can be observed in Fig. 2b. The size of these triangular pyramid QDs is around 5 nm and the diameter of nanopolymers is 80–200 nm. Fig. 2c exhibits the hexagonal nanopolymers obtained using 2 mL OA. The nanopolymers have a diameter of ca. 200 nm, which is much larger than the size of QDs. This will be discussed in detail later.

The crystalline nature of the CIS NCs can be further revealed by using HRTEM and SAED characterizations. Fig. 2d shows HRTEM image of CIS triangular pyramids obtained using 1 mL OA. It can be observed that all the distances of the lattice fringes are 0.32 nm, which is in good agreement with the distance between the (111) planes of zincblende phase. In addition, if the CIS pyramids are of zincblende phase, then the four facets should be (111) face,26,28 which is also consistent with the observation. Therefore, the CIS pyramids are of the zincblende phase exposed with (111) planes. The corresponding
SAED pattern is shown in Fig. 2g, and the ring pattern can be indexed to the (111), (220), (311), (400), (331) and (422) planes of zincblende CIS. So both zincblende phase and wurtzite phase are contained in the sample synthesized using 1.5 mL OA, which accords with the above XRD result. Fig. 2e shows HRTEM image of CIS triangular pyramids and hexagonal nanoplates synthesized using 1.5 mL OA. It is clear that the lattice fringes of the nanoplate with a distance of 0.34 nm correspond to (100) planes of wurtzite CIS, and the lattice fringes of the triangular pyramids with a distance of 0.32 nm are consistent with (111) planes of zincblende CIS. So both zincblende phase and wurtzite phase are contained in the sample synthesized using 1.5 mL OA, which accords with the above XRD result. Fig. 2f shows HRTEM image of CIS nanoplate obtained using 2 mL OA. The clear lattice fringes with a distance of 0.34 nm are consistent with (100) planes of wurtzite CIS. The SAED pattern (Fig. 2i) of the corresponding nanoplate reveals well single-crystalline nature of a nanoplate.

The valence states and composition of the as prepared CuInS2 nanocrystals were determined from XPS measurements. Two typical XPS spectra of pyramid nanoparticles and nanoplates are similar in Fig. 3. The full spectra in Fig. 3a show the presence of Cu 2p, In 3d and S 2p peaks, confirming the existence of these elements in the two samples. The binding energies of Cu 2p3/2 and Cu 2p1/2 are located at 932.5 eV and 952.3 eV with a peak splitting of 19.8 eV (Fig. 3b), in agreement with the reported values for Cu++. In addition, the copper Auger parameter is 1849.2 eV; it was calculated from the sum of the binding energy of the 2p3/2 XPS peak and the kinetic energy (KE) of the L3M45M45 Auger peak at 916.7 eV. Thus, copper oxidation state is thus +1 in the both samples.13 The In 3d peaks were located at 444.8 eV and 452.3 eV with a peak splitting of 7.5 eV (Fig. 3c), corresponding to In3+. In addition, the indium M4N45N45 Auger peak at 407.2 eV gives an Auger parameter of 852.0 eV, which suggests that the oxidation state of indium in the CuInS2 samples is +3. The S 2p peaks at 161.7 eV and 162.8 eV with a peak splitting of 1.1 eV in Fig. 3d match well with S2-. Through quantification of peaks, the molar ratios of Cu : In : S of pyramid nanoparticles and nanoplates are 1.30 : 1 : 1.95, and 1.61 : 1 : 2.46, respectively. Due to the large size of nanoplates, the above composition (Cu : In : S = 1.61 : 1 : 2.46) calculated from XPS result is probably
the elemental surface composition of CuInS$_2$ nanoplates, and thus deviates largely from the stoichiometric ratio. Therefore, EDX characterization was carried out and the result in Fig. S2 gives a Cu : In : S ratio of 1.30 : 1 : 1.83 for CuInS$_2$ nanoplates. It can be seen that, the both as-prepared samples are copper-rich with respect to the stoichiometric CuInS$_2$.

**Formation mechanism of CuInS$_2$ nanocrystals**

To investigate the effect of OA dosage on the CIS structures, the reaction process was observed and several samples were prepared. In our reaction system, CuCl, InCl$_3$·4H$_2$O were used as copper source and indium source, and DDT was used as sulfur source and surfactant. ODE was non-coordinating solvent and OA was served as co-capping agent. The OA dosage was tuned from 0 mL to 3 mL, and the total volume of OA and ODE was kept at 10 mL while the volume of DDT was fixed at 2 mL. It is said that DDT can easily react with certain metal salts, producing metal thiolates. In our reaction system, when CuCl, InCl$_3$·4H$_2$O, DDT, ODE and OA were mixed together at room temperature, a turbid white liquid containing metal thiolates were obtained. The metal thiolates were solved gradually during the heating process. When the temperature was kept at 100 °C, a clear solution was formed. It is interesting to note that the colours of the clear solutions are light yellow, yellow, brown and brown at the OA dosage of 0 mL, 1 mL, 2 mL, 3 mL, respectively, as shown in Fig. 4a. This is probably attributed to the state of intermediates affected by OA dosage. Then the clear solutions were heated to 200 °C gradually, and the colour of the solution began to change at 190 °C. At 0 mL OA, the colour of the clear solution is gradually turned from light yellow to brown and to dark brown as the reaction proceeds. At 1 mL and 1.5 mL OA, the colour is varied from yellow to brown and to dark brown. At 2 mL and 3 mL OA, the colour is turned from brown and to dark brown. The colour variation implies that intermediate compounds are formed by metal ions and DDT, and then these intermediates decomposed into CIS nanocrystals. Therefore, it is considered that the OA dosage affects the initial state of the intermediates and nucleation of CIS nanocrystals.

To determine the composition of the intermediates, XRD and FTIR characterizations were carried out for the samples taken out from reaction solution with 0 mL and 2 mL OA, respectively. As show in Fig. 4b, all the diffraction peaks match well with the XRD pattern of CuIn(SR)$_x$ complex, as suggested in the previous reports. XRD peak positions of the two intermediates are similar, while the intensities of low-angle peaks for the intermediates with 2 mL OA are much stronger than that without OA. In addition, there are more diffraction peaks for the intermediates with 2 mL OA than that without OA. This indicates that CuIn(SR)$_x$ complex is more stable in the mixture of OA and ODE than only in ODE. That is, high OA dosage can promote the formation and crystallization of CuIn(SR)$_x$ complex. To verify the intermediate formed, FT-IR spectra were measured for pure DDT, pure OA, pure intermediate, mixture of intermediate and CuInS$_2$ nanocrystals, and pure CuInS$_2$ nanocrystals, respectively (Fig. 5). It is shown that all samples have bands at 2925 and 2854 cm$^{-1}$, which is attributed to the C-H stretching vibration.
pure DDT and OA, the absence of the S-H vibration at 2572 cm⁻¹ and C=O vibration mode around 1550–1700 cm⁻¹ for the intermedie and CuInS₂ nanocrystals indicates that the formation of metal-sulfide bonds in these compounds does occur, and there are no metal oleates in the intermediate.²⁶

The formation and crystallization of CuIn(SR)ₓ complex promoted by a high OA dosage can be explained by the Hard–Soft-Acid-Base (HSAB) principle.²⁹ As is known, Cu⁺ and In³⁺ are soft and hard acids, respectively, and DDT is a soft base.²³ Usually, a soft acid tends to bind preferentially with a soft base rather than a hard base.²⁶ In this sense, DDT can coordinate well with Cu⁺ but cannot bind tightly with In³⁺ and thus it is difficult to form stable CuIn(SR)ₓ complex without OA or with low OA dosage. However, at high OA dosage, OA as a hard base can collaborate with DDT offering suitable coordination with In³⁺ to produce stable CuIn(SR)ₓ complex. This is in good agreement with the above results. According to the previous report,²⁴ stable CuIn(SR)ₓ complex as intermediates will lead to the formation of wurtzite CIS nanocrystals while unstable intermediates will be favourable for the production of zincblende CIS nanocrystals. In this sense, a high OA dosage will finally result in the formation of wurtzite CIS nanocrystals.

To further understand the growth mechanism of CIS NCs with different structures, CIS NCs synthesized using 0 mL and 2 mL OA at 200 °C at different reaction times were characterized by XRD. As shown in Fig. 6a, the XRD pattern of the sample taken out at the initial stage of nucleation (190 °C) is consisted of the diffraction peaks of zincblende CIS and CuIn(SR)ₓ complex (as shown in Fig. 4b). The sample contains both zincblende CIS NCs and CuIn(SR)ₓ complex. It can be found that, when the reaction time is prolonged, the diffraction peak intensity of zincblende CIS is increased while that of CuIn(SR)ₓ complex probably has completely converted into zincblende CIS due to their diffraction peak disappears. This indicates that CuIn(SR)ₓ complex is formed at first and then decomposed into zincblende CIS nuclei. The XRD pattern of the sample obtained at the initial stage of nucleation (190 °C) with 2 mL OA is presented in Fig. 6b. It can be found that the sample is consisted of wurtzite CIS and CuIn(SR)ₓ complex. But the content of wurtzite CIS is very small due to the relative low intensity of diffraction peaks. As the reaction continues, the CuIn(SR)ₓ complex is decomposed gradually and more wurtzite CIS is obtained (seen in Fig. 6b). However, the zincblende phase CIS emerges at 60 min and 90 min. From the TEM images (as shown in Fig. S1), it can be observed that a part of wurtzite nanoparticles is dissolved to form new zincblende nanoparticles because the zincblende CIS is thermodynamically more stable than the wurtzite CIS.¹²

As seen in Fig. 6, the relative intensity of diffraction peaks for CuIn(SR)ₓ complex using 2 mL OA was stronger than that without OA at the same reaction time, indicating that the formed CuIn(SR)ₓ complex is more stable in the reaction solution with 2 mL OA than that without OA. That is to say, the decomposition rate of CuIn(SR)ₓ in the solution without OA is faster than that with 2 mL OA. When the CuIn(SR)ₓ complex is comparatively stable, the low decomposition rate will lead to the formation of a few metastable wurtzite CuInS₂ nuclei. In addition, OA is also used as a surfactant and its capping ligands is selectively absorbed on the (002) facet of wurtzite CIS nuclei with higher surface energy, so the growth of (002) facet is inhibited and finally large nanoparticles are produced. Conversely, When the CuIn(SR)ₓ complex has a low crystallinity, the high decomposition rate can result in the large amounts of zincblende nuclei.¹⁸ But the growth rate of zincblende phase is slower than that of wurtzite phase due to the difference in the concentration of growth solution. This is because the production of zincblende nuclei can consume more metal ions in the reaction solution. Therefore, the size of zincblende CIS nanoparticles is small while wurtzite CIS nanoparticles have large size.

![Fig. 6 XRD patterns of CIS NCs taken out from the reaction solution with OA (a) 0 mL and (b) 2 mL OA at different times: 5 min, 10 min, 20 min, 60 min, 90 min at 200 °C; 190 °C was the initial stage of nucleation of CIS NCs.](image-url)
the state of CuIn(SR)\textsubscript{x} complex and nucleation rate of CIS NCs play a crucial role in determining whether the phase of CIS nuclei is zincblende or wurtzite. At a low OA dosage, the coordination of DDT and In\textsuperscript{3+} is weak, the formed CuIn(SR)\textsubscript{x} complex is not stable. In this sense, the CuIn(SR)\textsubscript{x} complex is easy to decompose and thus the nucleation rate is fast, resulting in a large amount of zincblende CIS nuclei. Because most of the metal monomers are consumed, the growth rate is slow and thus zincblende (ZB) CIS nanoparticles with small size are formed finally. On the contrary, when the OA dosage is high, OA can collaborate with DDT offering suitable coordination with In\textsuperscript{3+} to produce relatively stable CuIn(SR)\textsubscript{x} complex. And thus, the metal thiolates are difficult to decompose and the nucleation rate is slow, resulting in a small amount of wurtzite (WZ) CIS nuclei. The concentration of the metal monomers is high in the reaction solution, so the growth rate is fast and wurtzite CIS nanoplates with large size are synthesized. As the reaction continues, the obtained wurtzite nanoplates begin to be dissolved and new zincblende nanoparticles are generated. At a moderate dosage of OA, the nucleation rate and growth rate are moderate, producing both zincblende nanoparticles and wurtzite nanoplates.

<table>
<thead>
<tr>
<th>Dosage of OA</th>
<th>State of CuIn(SR)\textsubscript{x} complex</th>
<th>Nucleation rate</th>
<th>Nuclei</th>
<th>Growth rate</th>
<th>Product</th>
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<tr>
<td>low</td>
<td>unstable</td>
<td>fast</td>
<td>ZB CIS</td>
<td>slow</td>
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<tr>
<td>high</td>
<td>stable</td>
<td>slow</td>
<td>WZ CIS</td>
<td>fast</td>
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Scheme 1: Schematic formation mechanism of CIS nanocrystals using different OA dosages.

**Optical properties of CIS nanocrystals**

Optical properties of colloidal nanocrystals are of great importance for their potential applications as optoelectronic materials. It has been known that the optical properties of ternary NCs depend on their size, shape, composition, phase structure and surface states.\textsuperscript{22} The UV-vis absorption spectra of the as-prepared CIS NCs have been measured at room temperature and are shown in Fig. 7. It can be observed that there is a broad absorption in the visible region with a tail in the long-wavelength direction. And the absorption band moves to a longer wavelength as the volume of OA is increased from 1 mL to 2 mL. For the direct band gap semiconductor, the band gap can be determined by extrapolation from the linear region of a plot of (\(\alpha v\))^2 vs. hv (\(\alpha\)=absorption coefficient, \(h\)=Plank’s constant and \(v\)=frequency),\textsuperscript{24,36} by which it is estimated that the band gap of CIS NCs synthesized using 1 mL, 1.5 mL and 2 mL OA are 1.71 eV, 1.55 eV and 1.44 eV, respectively. It is reported that zincblende CuInS\textsubscript{2} has a band gap of 1.07 eV,\textsuperscript{23} which is much smaller than the experimental result 1.71 eV. This is because the zincblende CuInS\textsubscript{2} nanoplates have a smaller size of ca. 6 nm with respect to the excitation radius of CIS.\textsuperscript{21} The band gap of wurtzite CuInS\textsubscript{2} nanoplates with a large size is 1.44 eV, corresponding to the reported result.\textsuperscript{21,24} The CIS NCs synthesized using 1.5 mL OA have a band gap of 1.55 eV, which is attributed to the combination of zincblende CIS and wurtzite CIS.

![Absorption spectra of CIS NCs](image)

**Conclusions**

In conclusion, zincblende and wurtzite CuInS\textsubscript{2} nanocrystals were synthesized by a simple thermolysis of CuCl, InCl\textsubscript{3}·4H\textsubscript{2}O and DDT precursors in a non-coordinating solvent ODE with adjusting the OA dosage. OA plays a crucial role in the nucleation rate of CIS and puts important impacts on the structures of CIS nanocrystals. Zincblende CuInS\textsubscript{2} nanoparticles could be obtained at a low dosage of OA (< 1 mL) while a mixture of zincblende CuInS\textsubscript{2} nanoparticles and wurtzite CuInS\textsubscript{2} nanoplates formed at a moderate dosage of OA (~1.5 mL). When the OA dosage was high (2~3 mL), wurtzite CuInS\textsubscript{2} nanoparticles were produced but a part of them would be dissolved and transformed into new zincblende nanoparticles as the reaction proceeded. By studying the growth mechanism of CuInS\textsubscript{2} nanocrystals with different phase structures in detail, we suggest that the state of CuIn(SR)\textsubscript{x} complex and nucleation rate of CIS NCs can determine the phase structure of NCs. The CuIn(SR)\textsubscript{x} complex is unstable and the nucleation rate is fast, resulting in zincblende CIS QDs. When CuIn(SR)\textsubscript{x} complex is relatively stable and the nucleation rate is slow, wurtzite CIS nanoplates with larger size were obtained. More importantly, OA can help DDT coordinate with metal cations to form stable CuIn(SR)\textsubscript{x} complex as intermediates, thus reducing the decomposition rate of intermediates and then slowing down the nucleation rate of CuInS\textsubscript{2}. Our work will make a contribution to the control synthesis of other multi-component chalcogenide nanocrystals.

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Notes and references
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Electronic Supplementary Information (ESI) available: TEM and HRTEM images of CIS nanoparticles synthesized using 2 mL OA at 200 °C for 60 min. See DOI: 10.1039/b000000x/

CuInS$_2$ nanocrystals with different phase structures were synthesized by a facile heat-up method through simply adjusting the OA dosage. This is because, a high OA dosage could facilitate the formation and crystallization of the CuIn(SR)$_x$ intermediate, giving metastable wurtzite CuInS$_2$ structure, while low OA dosage would lead to low crystallinity of the intermediate, and thus transformation into zincblende CuInS$_2$ phase.

![Diagram showing the effect of OA dosage on the state of CuIn(SR)$_x$, nucleation rate, growth rate, and product.](image)

- Low OA dosage: unstable state → fast nucleation → ZB CIS → slow growth
- Moderate OA dosage: metastable state → moderate nucleation → ZB CIS, WZ CIS
- High OA dosage: stable state → slow nucleation → WZ CIS → fast growth (further growth indicated by upwards arrow)