

# One-dimensional growth of colloidal PbSe nanorods in chloroalkanes

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Catalyst-free, one-pot synthesis of colloidal PbSe nanorods is demonstrated. The co-solvent chloroalkanes play a critical role in driving a one-dimensional growth of PbSe nanorods. The formation of the nanorod is likely governed by the ani-

sotropic growth of the crystal due to the different reactivity of the facets. The photoluminescence quantum yield of the nanorods is above 25%, indicating well-passivated surfaces.

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**1 Introduction** Lead selenide (PbSe) represents a promising thermoelectric material owing to its high thermoelectric figure of merit [1–5]. This property is expected to be further enhanced in anisotropic one-dimensional structures [6, 7]. The employment of one-dimensional geometry in optoelectronic applications is also favorable for achieving a high carrier mobility and large diffusion length along the rod axis [8], in contrast to zero-dimensional quantum dots. Recent observation of high multiple-exciton-generation [9–12] rate and slow Auger recombination rate [13, 14] make them promising for highly-efficient photovoltaic devices.

Colloidal PbSe nanowires/nanorods have been synthesized previously by Cho and co-workers [15], where one-dimensional oriented attachment was identified to be the primary growth mechanism. Later, Koh and co-workers have developed a catalyst-free one-pot method to synthesize PbSe nanorods at lower reaction temperatures [16]. Han and coworkers introduced diphenylphosphine into the reaction, further reduced the reaction temperature and synthesized the nanorods with diameters ~2 nm [17]. By re-

moving the water from the reaction solution, Placencia and coworkers have demonstrated that branchless nanorods can be synthesized [18].

We developed a general method for the synthesis of PbSe nanorods using a chloroalkane (e.g. chloroform CHCl<sub>3</sub>) as the co-solvent during the reaction (see Supporting Information A). Chloroalkanes have been previously used to drive two-dimensional attachment of PbS quantum dots to form nanosheets [19–24]. The application of this co-solvent in the synthesis of PbSe was found to promote one-dimensional nanorods. The main focus of this Letter is to illustrate the effect of chloroalkanes on the growth of nanorods. We will also show that the as-synthesized PbSe nanorods have narrow photoluminescence peaks and high photoluminescence quantum yields that will find applications in infrared optoelectronics and photonics.

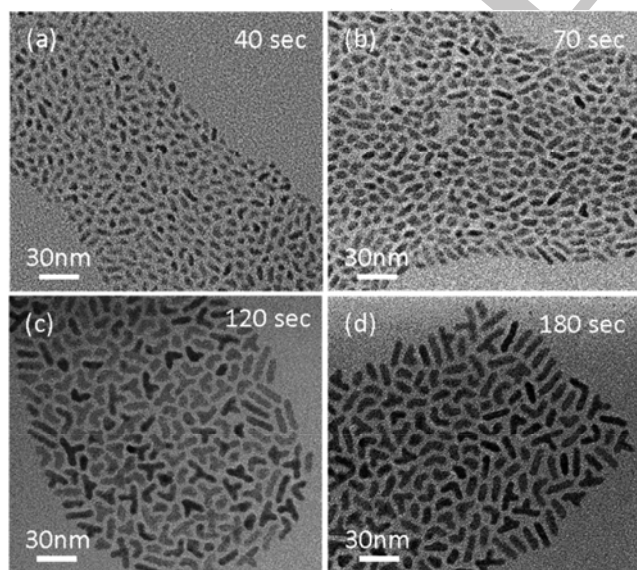
The role of the chloroalkanes in the shape-controlled syntheses of the colloidal nanostructures is not yet well understood. Chloroalkanes were originally thought to act as lead-complexing agents that modified the surface of the PbS nanocrystals and consequently altered the kinetics of

1 nucleation and growth [19]. The chloroalkane may also re-  
 2 lease  $\text{Cl}^-$  ions [25], which act as anionic X-type ligands to  
 3 bond to the metal ions on the nanocrystal and change its  
 4 growth dynamics [26], resulting in less-symmetric nano-  
 5 structures as demonstrated for CdS (rod shape) [27] and  
 6 CdSe (pyramidal shape) [26] nanocrystals. By performing  
 7 a crystallographic analysis of the intermediate structures  
 8 obtained at different reaction stages via transmission-  
 9 electron microscopy (TEM), we found that the aspect ratio  
 10 of the PbSe nanorods was nearly constant during the reac-  
 11 tion while the diameter of the rod increased over time. It  
 12 indicates that the nanorods are formed by the anisotropic  
 13 growth in a specific direction due to the chloroalkane. The  
 14 synthesized nanorods exhibit high photoluminescence  
 15 quantum yield, indicative of a good surface passivation  
 16 which may be attributed to the attachment of chloroalkane  
 17 molecules or Cl anions to the nanorod surfaces.

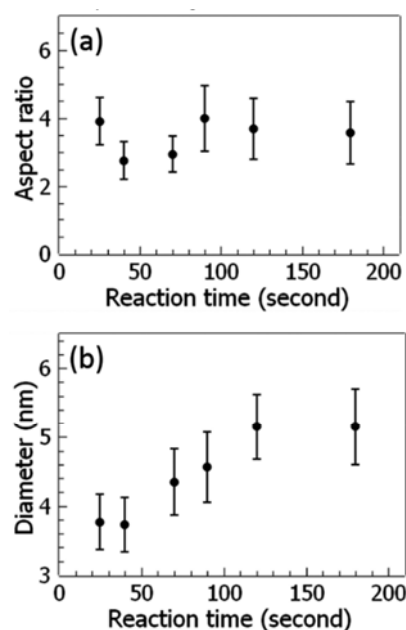
## 2 Experimental and results

20 **2.1 Growth mechanism** Unlike CdSe nanocrystals  
 21 which have a permanent dipole along the  $c$ -axis of the  
 22 crystal that drive the nanocrystal grow one-dimensionally  
 23 [28] the centrosymmetric PbSe nanocrystal has no intrinsic  
 24 dipole. However, non-centrosymmetric arrangements of  
 25 the polar  $\{111\}$  facets (either Se- or Pb-terminated) can re-  
 26 sult in a dipole moment along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  or  $\langle 111 \rangle$   
 27 axes, which will drive one-dimensional oriented attach-  
 28 ment of nanocrystals to form nanorods [15]. This is one  
 29 well-accepted mechanism explaining the growth of nano-  
 30 rods.

31 In our experiments, we observed the coexistence of  
 32 nanocrystals and nanorods at the early stage of the crystal  
 33 growth (see Supporting Information B and Fig. 1a). It is  
 34 possible that oriented-attachment occurs at this stage. After  
 35



55 **Figure 1** TEM images showing the growth of nanorods at differ-  
 56 ent stages. Reaction condition: 170 °C, 1,2,3-trichloropropane as  
 57 the chloroalkane co-solvent.

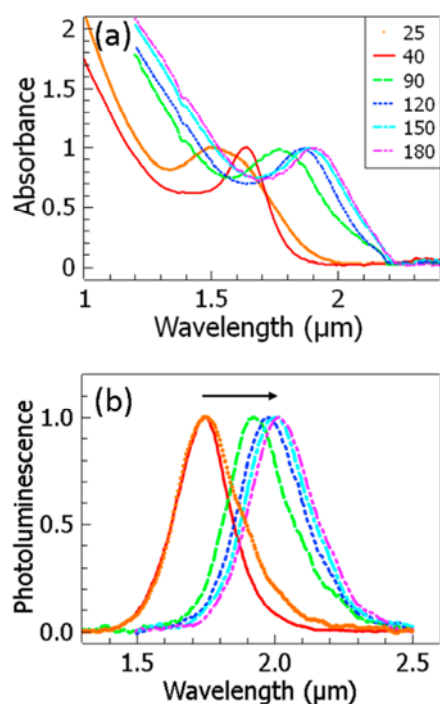


**Figure 2** (a) Aspect ratio of the nanorods versus the reaction time. (b) Average diameter of nanorods versus the reaction time. The error bars indicate the statistic errors ( $\pm$  standard deviation).

70 seconds, nearly all nanocrystals developed into I-shaped, L-shaped or T-shaped nanorods. From that point on (70 seconds into the growth), the aspect ratio of the I-shaped nanorods remained nearly constant while the diameter of the nanorods increased over the reaction time (Fig. 2). The increase of the diameter of the nanorods by reaction time (Fig. 2b) is similar to that observed in Koh's syntheses [16]. The nearly constant aspect ratio  $\sim 4$  in our synthesis (Fig. 2a) indicates that the axial growth rate is about 4 times of the lateral growth rate. However, one-dimensional oriented attachment of the nanocrystals in Koh's synthesis additionally increases the axial growth of the nanorods, resulting in an increase of the aspect ratio of the nanorods by reaction time [16]. That process is different from what was observed in our syntheses where oriented attachment is likely missing.

As the reaction time increases, the increase in the nanorod diameter is accompanied by the reduction in the band gap. Both the absorption and photoluminescence measurements consistently show this trend (Fig. 3), manifested by the spectral red-shift of the respective excitonic features. After about 120 seconds, the diameter of the nanorods remains nearly the same (Fig. 2b), indicating that the monomers have been consumed and the nanorods stop growing.

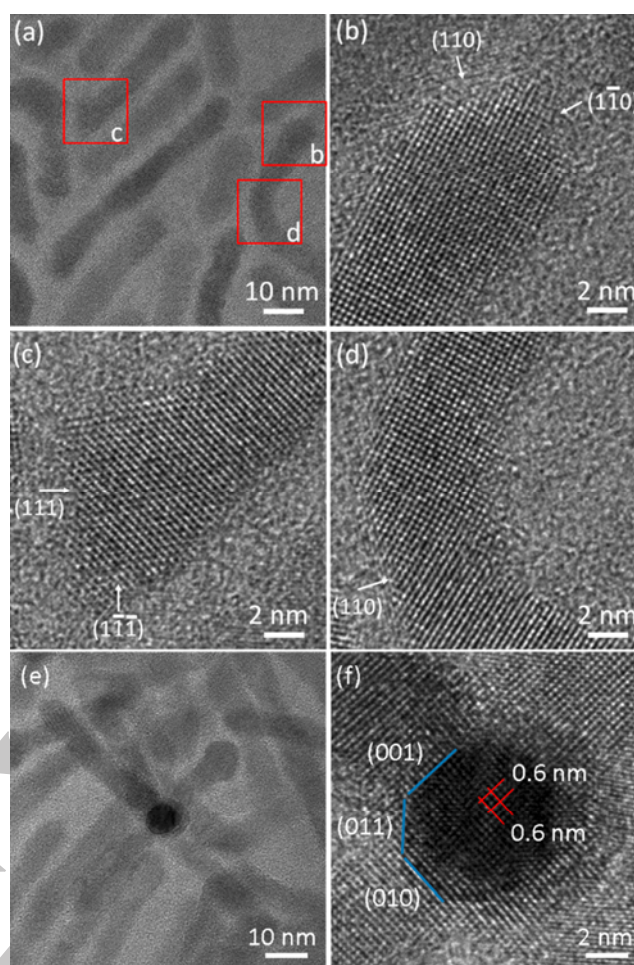
High-resolution TEM (HRTEM) was used to further understand the crystal structure and the anisotropic growth of the PbSe nanorods. The images of nanorods in Fig. 4 shows that their side facets are either  $\{100\}$  (Fig. 4b) or  $\{110\}$  (Fig. 4c). It indicates that the axis of the nanorod is in either  $\langle 100 \rangle$  or  $\langle 110 \rangle$  direction. Further analysis of the HRTEM image shows that the projected minimum atom



**Figure 3** (a) Absorbance spectra of the PbSe nanorods at different growth stages. Inset: the symbols and the corresponding reaction times in seconds. (b) Photoluminescence spectra of PbS nanorods at different reaction times indicated by the same symbols as in (a). The arrow shows the red-shift of the photoluminescence peak by the reaction time.

spacing is 0.31 nm (Fig. 4b, c) in the axial direction, 0.31 nm (Fig. 4b) or 0.22 nm (Fig. 4c) in lateral direction. These are unique features of the nanorod with its axis in  $\langle 100 \rangle$  direction (Supporting Information C). Nanorods with its axis in  $\langle 110 \rangle$  direction also show  $\langle 100 \rangle$  or  $\langle 110 \rangle$  side facets, but the projected minimum atom spacing in axial or lateral direction will be different.

Based on the HRTEM images, we find that the two ends of nanorods are not flat but exhibit sharp tips. In the zone axis  $\langle 001 \rangle$ , the angle is  $90.0^\circ$  (Fig. 4b), while in the zone axis  $\langle 110 \rangle$ , the angle is  $70.5^\circ$  (Fig. 4c) (Supporting Information D). It reveals that the ends of nanorods are dominated by  $\{110\}$  and  $\{111\}$  facets. The  $\{110\}$  and  $\{111\}$  facets are more reactive than  $\{100\}$  facets due to a higher density of dangling bonds [28]. We speculate that the growth in the  $\langle 110 \rangle$  and  $\langle 111 \rangle$  directions results in a net growth in  $\langle 100 \rangle$  direction. As shown in Fig. 4b, the growths of the  $(110)$  and  $(1\bar{1}0)$  facets are in  $[110]$  and  $[\bar{1}\bar{1}0]$  directions, respectively. They make a right angle. The components in  $[010]$  and  $[0\bar{1}0]$  (perpendicular to the rod axis) are opposite to each other. The competition among them limits the crystal growth in the radial directions. However, the components in  $[100]$  direction add up so that the growth in the  $[100]$  direction is enhanced. The growth of  $(111)$  and  $(\bar{1}\bar{1}\bar{1})$  facets (Fig. 4c) follows the same mechanism and results in a net growth in  $[\bar{1}00]$  direction. The different growth rate in  $(111)$  and  $(\bar{1}\bar{1}\bar{1})$  facets results



**Figure 4** (a) A TEM image of PbSe nanorods synthesized at  $180^\circ\text{C}$  with TCP. The squares labeled with “b”, “c” and “d” indicate the areas to be zoomed-in in (b), (c) and (d), respectively. (b) A HRTEM image of the nanorod showing a rock-salt crystal structure with  $\{100\}$  facet facing up. The tip of the rod is formed by the  $(110)$  and the  $(\bar{1}\bar{1}0)$  facets. (c) A HRTEM image of the nanorod with its  $\{110\}$  facet facing up. The tip of the rod is formed by  $(111)$  and  $(\bar{1}\bar{1}\bar{1})$  facets. (d) The HRTEM image of an L-shaped nanorod with its  $(100)$  facet facing up. The growth direction of the nanorod make two  $45^\circ$  turns, making an L-shaped nanorod. (e) A HRTEM image showing a nanorod pointing upward as the others lying down on the substrate. (f) The HRTEM image of the tip of the PbSe nanorod showing a  $(100)$  facet.

in different sizes of the two facets. As shown in Fig. 4c, facet  $(111)$  is much larger than facet  $(\bar{1}\bar{1}\bar{1})$ . When the difference is large enough, the growth direction will change. As shown in Fig. 4d, the initial growth direction  $[100]$  turns to  $[110]$  and then  $[010]$ , making an L-shaped rod.

Notably, the observed one-dimensional growth is only possible when a chloroalkane is used as the cosolvent during the reaction. If it is absent, nanocrystals evolve to hexapods or octahedrons (Supporting Information E), which are not emissive. Similar nanostructures have been reported earlier by Houtepen [29], Gerdes [30] and co-

workers. Gerdes and coworkers mentioned that each branch of the hexapod extends in  $\langle 100 \rangle$  direction [29]. The presence of chloroalkanes slows down the nucleation and the formation of the nanocrystals [29, 31]. Chloroalkanes are considered to be a lead-complexing agent [19, 29] which is likely the cause of the slow nucleation and growth of nanocrystals. The slow growth makes it possible for the  $\{110\}$  and  $\{111\}$  facets to manifest their higher reactivity (due to their higher density of dangling bonds than  $\{100\}$  facets) [28], resulting in the net growth of the nanocrystal in  $\langle 100 \rangle$  direction as mentioned earlier. Interestingly, the type of chloroalkane has no noticeable effect on the growth of nanorods. A series of chloroalkanes (chloroform, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,2-dichlorobutane and 1,2,3-trichloropropane) have been tested for the synthesis and the same growth kinetics were observed.

There are six equivalent  $\langle 100 \rangle$  directions for a cubic crystal. In principle, it can grow into a star-shaped structure with six long arms. The prevailing I-shaped rods indicates that they are not exactly equivalent. Some facets are slightly more reactive than others so they dominate the growth direction. However, growth in other directions is also possible when the reactivity of each facet are nearly the same. This results in an L-shaped, T-shaped (Fig. 1) and even six-arm star-shaped (Fig. 4) structures. In these structures, some arms point upward from the TEM grid, making it possible to observe the crystal structure along the rod axis (Fig. 4e, f). The dark octagonal spots (Fig. 4f) are commonly seen in the HRTEM images, so they are unlikely due to the random overlaps of two or more individual nanorods. The HRTEM image (Fig. 4f) confirms that the end facet is  $\{100\}$ , and other arms extend in  $\langle 100 \rangle$  directions as well. The image also reveals that the cross-section (perpendicular to the axis of the rod) of the rod is octagonal. The octagonal rod likely grows from a cuboctahedron (or truncated octahedron) seed [32], a typical shape of a PbSe [33] or PbS [34, 35] nanocrystal.

The branching of the nanorods is important for us to study the growth mechanism, but it could be suppressed by removing the excess water and acetic acid in the reaction solution. Placencia [18] and Boercker [36] have demonstrated that removing water in the reaction solution suppressed branching of PbSe nanorods. We expect that it might work in our synthesis as well.

It is worthy to note that the chloroalkanes make PbSe grow one-dimensionally in this work, but make PbS grow two-dimensionally [19–21]. We suspect that the subtle difference of the Se and S chemistry might be the cause. It is an on-going project in our group to solve this puzzle.

**2.2 Optical properties** Overall, the final product contains PbSe nanorods that are uniform in diameter as manifested by a relatively narrow photoluminescence emission peak (Supporting Information F). The ratio of the full-width at half-maximum to the central photon energy is typically less than 0.14. This implies the dispersion of the

energy gap or the diameter is within  $\pm 7\%$ . The absolute photoluminescence quantum yield was measured using an integrating sphere [37], following the method developed by Friend et al. [38]. The nanorods with an energy gap of 0.8 eV have the quantum yield about 27%, nearly twice as much as the quantum yield (15%) of the nanorods synthesized by Koh and coworkers [16]. The high quantum yield is likely due to the additional surface passivation by the chloroalkane since the energy-dispersive X-ray spectroscopy of nanorods shows Cl peak (Supporting Information G). This result is consistent with an earlier study by Tang and coworkers who demonstrated that the performance and the stability of the PbS quantum-dot solar cells were enhanced after passivating the quantum-dot surface using halide anions (including  $\text{Cl}^-$ ) [39].

**3 Conclusions** In summary, we have investigated the effect of chloroalkanes on the growth of PbSe nanorods. The chloroalkane co-solvent is critical for the formation of the one-dimensional nanostructures. They also improve the surface passivation for the nanorods, resulting in a high photoluminescence quantum yield. The developed approach with the application of chloroalkanes provides a new route for the synthesis of high-quality colloidal PbSe nanorods which may find applications in infrared photonics and optoelectronics.

**Supporting Information** Additional supporting information may be found in the online version of this article at the publisher's website.

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