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Facile Solution-Phase Synthesis of CuInSe₂ Nanocrystals with Controlled Morphologies

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The morphology of CuInSe₂ nanocrystals plays a key role in their functional properties. Achieving controllable morphology is significant for studying their structures and novel properties. Here, CuInSe₂ nanocrystals with a trigonal-pyramidal shape have successfully been synthesized by a facile solution-phase method. The nanocrystals were characterized by X-ray diffraction (XRD), transmission electron microscopy

Introduction

Semiconductor nanocrystals have been the object of intensive scientific and technological interest.^[1] They exhibit outstanding optical, electronic, thermal, and magnetic properties that are different from the bulk materials because of their quantum-confinement effects and size-dependent photoemission characteristics.^[2] In recent years, the I-III-VI family of semiconductor nanocrystals, which consists of I (Cu, Ag), III (Ga, In), and VI (S, Se, Te) have been regarded as promising solar-cell and biolabeling materials because of their low toxicity, optimal band gaps that are well matched with the solar spectrum, large light absorption coefficient, large Stokes shift, and emission wavelengths in the near-infrared region.^[3] Among the I-III-VI family, CuInSe₂ exhibits thermodynamic stabilization at room temperature, a direct band gap of 1.03-1.10 eV (in the bulk phase) and a Bohr excitation radius of 10.6 nm as previously reported. It has been considered as an absorbed layer material of solar cells with excellent performance.^[4] Furthermore, CuInSe₂ nanocrystals, which may produce large numbers of P-N junctions, are expected to be able to greatly improve the conversion efficiencies of thin-film solar cells.^[5] In addition, CuInSe₂ nanocrystals in the strong quantum con(TEM), and X-ray photoelectron spectroscopy (XPS), etc. The morphological evolution of the CuInSe₂ nanocrystals was illustrated by tuning the injection temperature of oleylamine-selenium (OAm-Se). In addition, CuInSe₂ nanocrystals with spherical and ellipsoidal shapes were also obtained when copper stearate was used as the copper precursor.

finement regime ($d \ll 2a_{\rm B}$; d is the diameter of the nanocrystals, $a_{\rm B}$ is the exciton Bohr radius) are predicted to be luminescent emitters in the red and near-infrared region.^[6] So far, many groups have reported CuInSe₂ nanocrystals with excellent shape, dispersion, and quality.^[4,7–14] Korgel et al. synthesized monodisperse CuInSe2 nanocrystals with trigonal-pyramidal shapes from the solution-phase route using selenourea as the selenium precursor.^[11] Schoen et al. synthesized CuInSe2 nanowires by vapor-liquid-solid (VLS) techniques.^[12] Guo et al. synthesized CuInSe₂ nanocrystals with nanoring inks for low-cost solar cells, and the efficiency of the cell is 2.8% under standard AM 1.5 illumination.^[13] Furthermore, wurtzite CuInSe₂ nanocrystals were first synthesized by Brutchey's group.^[4] It is noteworthy that morphology is a key parameter in the design of CuInSe₂ nanocrystals with controlled functional properties. Despite the success in the synthesis of CuInSe₂ nanocrystals, tuning the morphology of CuInSe₂ nanocrystals is still rare. Here, we have a great interest in the trigonal-pyramidal CuInSe₂ nanocrystals reported by Korgel et al.^[11] Inspired by their report, we speculate that if we can slow down the growth rate along the [112] direction, precise control of the shape of the $CuInSe_2$ nanocrystals may be achieved.

In this paper, we report a facile route to synthesizing $CuInSe_2$ nanocrystals with a trigonal-pyramidal shape. Cuprous chloride, indium stearate, and OAm-Se were used as copper, indium, and selenium precursors, respectively. Monodisperse chalcopyrite $CuInSe_2$ nanocrystals with a trigonal-pyramidal shape were obtained. Subsequently, the shape of $CuInSe_2$ nanocrystals gradually evolved into a cut-away octahedron by tuning the injection temperature from 210 °C to 130 °C. In addition, we also attempted to use copper stearate instead of cuprous chloride. Spherical CuInSe₂

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nanocrystals were obtained, and the shape could be evolved into ellipsoidal by changing the volume of oleylamine (OAm) from 1 mL to 3 mL.

Results and Discussion

CuInSe₂ nanocrystals shown in Figure 1a were produced by injecting OAm-Se into a preheated mixture of OAm. Cuprous chloride and indium stearate were maintained at 210 °C, while the reaction temperature was also maintained at 210 °C. Upon injection, the color of the reactive system turned brown rapidly, indicating that nucleation had occurred, and the nanocrystals began to grow. The reaction stopped after 5 min. Figure 1a shows the TEM image of the CuInSe₂ nanocrystals with a triangular shape. The nanocrystals have an average length of 13.5 nm on two sides and 14.5 nm on the other side (Figure S1). The three major rings of the electron diffraction (ED) pattern shown in Figure 1b correspond to the (112), (204)/(220), (116)/(312) reflection direction of the as-synthesized CuInSe₂ nanocrystals. The high-resolution TEM (HRTEM) image of an individual nanoparticle, as shown in Figure 1c, displays high crystallinity for CuInSe₂ nanocrystals. The distance between the adjacent atomic lattice fringe is about 3.34 Å and 2.04 Å, which is consistent with the (112) and (220) planes, respectively, of chalcopyrite CuInSe₂. Both the electron diffraction (ED) patterns and the HRTEM images confirm that the particle has a single-crystalline feature. Phase structures of the as-synthesized CuInSe₂ nanocrystals were investigated by XRD. Figure 1d shows the XRD pattern of CuInSe₂ nanocrystals with a triangular shape and the standard data for chalcopyrite-phase CuInSe₂ as well. All diffraction peaks are in good agreement with the bulk CuInSe₂ (JCPDS 40-1487). The major diffraction peaks can be indexed as (112), (204)/(220), (116)/(312), (008)/(400), and (316)/ (332). The average crystalline sizes are estimated as 14.3 nm by the Scherrer equation from the XRD diffraction peaks, which are consistent with the results from TEM images. XPS was used to confirm the composition and valence states of the CuInSe₂ nanocrystals with a trigonal-pyramidal shape (Figure S2). All the measurements were carried out with reference to the C1s binding energy (BE) (284.6 eV) as an internal standard. Figure S2a shows the photoelectron spectra of the as-prepared products over a wide range of binding energies. It is very clear that Cu, In, Se, C, O are the only prominent elements present in the sample. Detailed XPS spectra of Cu2p3/2, Cu2p1/2, In3d5/ 2, In3d3/2, and Se3d binding energies for nanocrystals are shown in Figure S2b-d, respectively. The BE values of Cu2p3/2 and Cu2p1/2 are 931.8 eV and 951.8 eV, respectively, for our sample, in good agreement with Cu⁺ that has been reported elsewhere.^[15] Furthermore, Cu²⁺ with a binding energy of 942 eV has not been observed. Therefore, we can confirm that only monovalent copper exists in the CuInSe₂ nanocrystals.^[16] The peak of In3d located at 444.5 eV and 451.95 eV, and the Se3d peaks located at 54.1 eV indicate In³⁺ and Se²⁻, respectively.^[9] X-ray (EDX) analysis further confirms the local element composition of CuInSe₂ nanocrystals (Figure S3).



Figure 1. (a) TEM images of $CuInSe_2$ nanocrystals. (b) ED patterns of the as-synthesized $CuInSe_2$ nanocrystals. (c) HRTEM images of $CuInSe_2$ nanocrystals. (d) XRD patterns for the $CuInSe_2$ nanocrystals. Literature values for the peak positions and intensities for bulk chalcopyrite (tetragonal) $CuInSe_2$ samples are indicated by the vertical bars.

The absorption spectra of the as-synthesized triangular CuInSe₂ nanocrystals in a toluene solution are shown in Figure 2. The band gap of the triangular CuInSe₂ nanocrystals was determined to be 1.14 ± 0.02 eV, which is basically in agreement with the reported 1.04-1.10 eV for bulk chalcopyrite CuInSe₂.^[3a,4] Compared with the bulk chalcopyrite CuInSe₂, whose absorption onsets at about 1200 nm, the absorption band edge of the as-synthesized CuInSe₂ nanocrystals does not display a blueshift because of quantum confinement, suggesting that the as-synthesized nanoparticles are not small enough.^[13]

The CuInSe₂ nanocrystals observed by scanning electron microscopy (SEM) (Figure S4) have a trigonal-pyramidal shape. We believe the morphology of our as-synthesized CuInSe₂ nanocrystals is similar to that in the report by Korgel and co-workers.^[11] According to their demonstration, the trigonal-pyramidal CuInSe₂ nanocrystals are bound by three $\{114\}$ and one $(\overline{112})$ surface facets. In addition, an opposing (112) surface is correspondingly unstable and leads to fast growth in the [112] direction. We thought that if the fast growth rate along the $[11\overline{2}]$ direction is restrained, the shape of the nanocrystals could be changed. The traditional method to control the shape of nanocrystals is usually to tune the amount of the surfactant directly, but we achieved this purpose by tuning the injection temperature of OAm-Se, while keeping the other parameters fixed. Figure 3a-c shows the TEM images with an injection temperature of 190 °C, 160 °C, and 130 °C, respec-





Figure 2. UV/Vis absorption spectrum of the as-synthesized Cu-InSe₂ nanocrystals. The band gap of the nanocrystals is approximated by using the direct band gap method plotting the absorbance squared vs. energy, and extrapolating to zero as shown in the inset.

tively. It is interesting to note that the shape of the CuInSe₂ nanocrystals gradually evolved into hexagons. According to Pang and co-workers,^[17] injection and growth temperatures are crucial factors in tuning the balance between nucleation and growth. For our synthesis system, when the injection temperature is decreased, the initial nucleation rate is slower so that the amount of crystal nuclei is less. If the amount of crystal nuclei is less, a relatively high concentration of OAm would bind to the crystal faces, and further suppress the growth rate along the [112] direction. A similar phenomenon, which we have speculated on, also happened for the growth along three other directions [114], [114], [114]. And then the CuInSe₂ nanocrystals with a cutaway octahedral shape (Figure S5) appeared when the injection temperature reached 130 °C, as shown in Figure 3c. In order to further testify the relationship between injection temperature and the amount of nucleation, we prolonged the reaction time when the injection temperature was 210 °C (Figure S6), but the size of the nanocrystals exhibited almost no change. This indicates that there were few residual monomers for the growth of the nanocrystals, and most were used for the nucleation of nanocrystallites. Herein, we can control the shape of the as-synthesized nanocrystals by tuning the injection temperature of OAm-Se.

When the Cu precursor was changed to copper stearate, OAm-Se was injected into the preheated mixture at 130 °C, while maintaining the reaction temperature at 210 °C. After 1 h, spherical CuInSe₂ nanocrystals were prepared, as shown in Figure 4a. The phase structures of the as-prepared products were investigated by XRD (Figure S7). The three major peaks are in good agreement with the bulk chalcopyrite CuInSe₂ crystal phase (JCPDS 40-1487). But there are some other small diffraction peaks in the XRD patterns, and the same phenomenon also occurs in the ED patterns (Figure S8). We speculate that they could be attributed to CuSe (JCPDS 49-1457) and wurtzite CuInSe₂ as reported.^[4] The average diameter of the nanocrystals calculated by the Scherrer equation from the XRD diffraction peaks was 24.8 nm, which basically agrees with the average size shown



Figure 3. TEM images of CuInSe₂ nanocrystals with the injection temperature of Se/OAm at (a) 190 °C, (b) 160 °C, (c) 130 °C. All scale bars are 50 nm.

in Figure S9. When we increased the volume of OAm to 3 mL, the shape of the CuInSe₂ nanocrystals changed to ellipsoidal as shown in Figure 4b. The HRTEM image of an individual spherical and ellipsoidal shape displays high crystallinity for CuInSe₂ nanocrystals (Figure 4c–d). The distance between the adjacent atomic lattice fringe is about 3.36 Å and 3.35 Å, which is consistent with the (112) planes of the chalcopyrite CuInSe₂. We consider that the divalent copper atom was reduced by OAm, which is similar to that reported by Xie and co-workers where OAm is used as the reducing agent instead of ethylenediamine.^[8] In addition, we believe that the high concentration of OAm can bind to certain crystal faces more strongly so as to block the growth of them as a result of the difference in the growth rate for different crystal faces. In Figure 4, we can clearly observe the shape of the CuInSe₂ nanocrystals that have changed from spherical to ellipsoidal. Consequently, it is easy to understand that the OAm plays an important role not only in assisting the formation of the CuInSe₂ nanocrystals but also in controlling the nanocrystal morphologies.





Figure 4. TEM images of $CuInSe_2$ nanocrystals synthesized with (a) 1 mL of OAm, and (b) 3 mL of OAm, and their typical HRTEM images in (c) and (d), respectively.

Conclusions

Monodisperse chalcopyrite $CuInSe_2$ nanocrystals with a trigonal-pyramidal shape were synthesized by a facile hotinjection method. The morphology could be tuned by changing the injection temperature. The reason for the morphological evolution could be that the injection temperature affects the crystal nucleus, and further affects the effect of OAm on the growth rate along the different directions, which realizes the shape evolution. In addition, CuInSe₂ nanocrystals with a spherical shape were also obtained when copper stearate was used as the copper precursor. Because of the binding effect of OAm, an ellipsoidal shape was also obtained when increasing the concentration of OAm.

Experimental Section

Materials: Oleylamine (OAm, 70%) and selenium powder (Se, 99.99%) were purchased from Sigma–Aldrich. Copper(II) nitrate trihydrate (99.0–102.0%), indium(III) nitrate hydrate (99.5%), and oleic acid (OA) were obtained from Sinopharm Chemical Reagent Co., Ltd. 1-Octadecene (ODE, 90%) was purchased from Alfa Aesar. Copper(I) chloride (AR) was purchased from the Beijing Chemical Reagents Company. Sodium stearate was purchased from the Shanghai Chemical Reagents Company. All chemicals were used as received without further treatment.

Synthesis of CuInSe₂ Nanocrystals with a Trigonal-Pyramidal Shape: The CuInSe₂ nanocrystals were synthesized by the hot-injection method. An OAm-Se stock solution was first prepared by dissolving Se (40 mg, 0.5 mmol) in OAm (5 mL); this solution was heated at 200 °C under Ar for 2 h, and kept in a vacuum oven at 70 °C. The synthesis method of copper stearate and indium stearate is described in the Supporting Information. In a typical synthesis, cuprous chloride (4.95 mg, 0.05 mmol), indium stearate (48.8 mg, 0.05 mmol), and OAm (4 mL) were mixed together in a 50 mL three-neck flask, which was connected to a Schlenk line and degassed at room temperature for a while followed by purging with Ar under magnetic stirring. Subsequently, the mixture was heated to 130 °C under Ar for 30 min. When the initial colorless solution turned bright-yellow, the mixture was continuously heated to 210 °C. An OAm-Se (1 mL) stock solution was injected rapidly into the hot mixture and the temperature kept at 210 °C; the reaction solution turned dark-brown instantly. After 5 min, the products were cooled to room temperature to yield CuInSe₂ nanocrystals. The products were precipitated by the addition of methanol followed by centrifugation at 5000 rpm for 5 min, and the precipitate was redispersed in a toluene solution.

Synthesis of CuInSe₂ Nanocrystals with a Spherical Shape: In a typical experimental synthesis, copper stearate (31.5 mg, 0.05 mmol) was used instead of cuprous chloride. OAm (1 mL) and ODE (3 mL) were used instead of OAm (4 mL). The injection temperature of the OAm-Se (1 mL) stock solution was 130 °C, and the reaction time was 1 h. All the other conditions were the same as those in the above description.

Materials Characterization: An XRD analysis was performed with a Rigaku D/max-2500 diffractometer with a graphite monochromator by using Cu- K_a radiation operating at 200 mA and 40 kV. XRD data were collected over the range of 20–80° (2 θ) with a step interval of 0.02° and a preset time of 1.6 s per step at room temperature. TEM and HRTEM images were performed with a FEI Tecnai G2 S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally with a Gantan multiple CCD camera. EDX spectra were obtained with a JEOL JSM 6700F instrument. The surface of the CuInSe₂ nanocrystals was characterized by XPS, recorded with an ESCALAB 250 X-ray photoelectron spectrometer by using Mg- K_a X-rays as the excitation source. SEM was performed with a FEI Helios 600i. UV/Vis/NIR absorption spectra were measured with a Shimadzu UV-3600 spectrophotometer.

Supporting Information (see footnote on the first page of this article): XPS, EDX spectra, SEM, TEM images and XRD profile.

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