

Electronic Supplementary Information

Phase-controlled synthesis of orthorhombic and tetragonal AgGaSe₂ nanocrystals with high-quality

Tianyu Bai,^{*a} Shanghua Xing,^b Chunguang Li,^b Zhan Shi,^{*b} and Shouhua Feng^b

^a College of Medical Laboratory, Dalian Medical University, No. 9 West Section LvShun South Road, Dalian 116044, P. R. China

E-mail: bty16@dmu.edu.cn

^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R. China

E-mail: zshi@jlu.edu.cn

Experimental Detail

Materials. Selenium powder (Se, 99.99%) and oleylamine (OAm, 70%) were purchased from Sigma-Aldrich. Sodium stearate, oleic acid (OA, 90%) and 1-Octadecene (ODE, 90%) was obtained from Alfa Aesar. Silver(I) nitrate (>99.8%), Gallium(III) nitrate nonahydrate (99.99%), indium(III) nitrate hydrate (99.5%) and thiourea (TU, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemical were used as received without further treatment.

Synthesis of gallium(III) stearate and indium(III) stearate. In a typical synthesis of gallium(III) stearate, sodium stearate (1.84 g, 6 mmol.) was added in 400 mL of distilled water and the water was heated to dissolve the sodium stearate. Then, an aqueous solution containing gallium(III) nitrate nonahydrate (0.836 g, 2 mmol) was dropwise added into the above hot solution under stirring. When the reaction was completed, the hot mixture containing gallium(III) stearate was filtered and washed three times with hot water. After washing, the white precipitate was dried, resulting in gallium(III) stearate in a waxy solid form. The synthesis of indium(III) stearate is similar as the gallium(III) stearate, using indium(III) nitrate hydrate (0.764 g, 2 mmol) instead of gallium(III) nitrate nonahydrate.

Synthesis of orthorhombic AgGaSe₂ nanocrystals. Oleylamine-selenium (OAm-Se, 0.2M) stock solution was first prepared by dissolving Se (158 mg, 2 mmol) in OAm (10 mL). This solution was heated at 200 °C for 2 hours under Ar gas, and kept in a vacuum oven at 70 °C. For a typical synthesis, silver(I) nitrate (17 mg, 0.1 mmol), gallium(III) stearate (92.2 mg, 0.1 mmol), OAm (8 mL) and OA (1 mL) were mixed together in a 50 mL three neck flask, which is connected to a Schlenk line and degassed at room temperature for 20 minutes followed by purging with Ar gas under magnetic stirring. Subsequently, the mixture was heated to 130 °C. When the initial colorless solution turned bright yellow, the OAm-Se (2 mL) stock solution was injected into the mixture. The color of the mixture rapidly turned dark brown, indicating the formation of the nuclei. Next, the mixture was heated to 280 °C and held at this temperature for 2 hours, during which the color of the mixture gradually changed from dark brown to dark red. Finally, the products were cooled to room temperature to yield AgGaSe₂ nanocrystals. Methanol was added to precipitate the nanocrystals and then the products were collected by centrifuge at 8000 rpm for 10 minutes. The precipitate was redispersed in toluene.

Synthesis of orthorhombic AgXY₂ (X = In, Ga; Y = S, Se) nanocrystals. The preparation method of orthorhombic AgXY₂ (X = In, Ga; Y = S, Se) nanocrystals was similar to the AgGaSe₂ nanocrystals. In a typical synthesis, silver(I) nitrate (17 mg, 0.1 mmol), indium(III) stearate (97.6 mg, 0.1 mmol) or gallium(III) stearate (92.2 mg, 0.1 mmol), OAm (8 mL) and OA (1 mL) were mixed together, and the mixture was heated to 130 °C. OAm-Se (0.2 M) or OAm-TU (0.2 M, prepared by dissolving 2 mmol of thiourea in 10 mL of OAm at 160 °C for 2 hours under Ar) was injected into the mixture. Next, the mixture was heated to 280 °C and held at this temperature for 2 hours. Finally, the products were cooled to room temperature. Methanol was added to

precipitate the nanocrystals and then the products were collected by centrifuge at 8000 rpm for 10 minutes. The precipitate was redispersed in toluene.

Material characterization. Powder X-ray diffraction (XRD) analysis was performed on a Rigaku D/max-2500 diffractometer with a graphite monochromator by using Cu-K α radiation operating at 200 mA and 40 kV. XRD data were collected over the range 20-70° (2θ) with a step interval of 0.02° and a preset time of 1.6 s per step at room temperature. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a FEI Tecnai G2 S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally on a Gantan multiple CCD camera. Energy dispersive X-ray (EDX) spectra were obtained using a JEOL JSM-6300 at 5 kV. The surface of the AgXY₂ (X = In, Ga; Y = S, Se) nanocrystals was characterized by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 X-ray photoelectron spectroscope, using Mg K α X-ray as the excitation source. UV-vis-NIR absorption spectra were measured with a Shimadzu UV-3600 spectrophotometer.

Table S1. Comparison of experimental and simulated d-spacings for orthorhombic AgGaSe₂ NCs

h	k	l	Simulated d-spacing (Å)	Experimental d-spacing (Å) ^a
1	2	0	3.560	3.559
2	0	0	3.412	
0	0	2	3.335	3.329
1	2	1	3.141	3.148
2	0	1	3.038	
1	1	2	2.820	2.827
1	3	0	2.576	2.578
0	3	1	2.568	
1	2	2	2.434	2.428
2	0	2	2.385	
2	1	2	2.293	
0	4	0	2.087	2.091
3	2	0	1.997	2.012
1	2	3	1.886	1.895
2	0	3	1.863	
2	4	0	1.780	1.775
0	4	2	1.769	
3	2	2	1.714	1.726
4	0	1	1.653	1.663
2	4	2	1.570	1.576

^a d-spacing of all the distinct visible peaks from the XRD pattern.

Cryst data

Formula: AgGaSe₂

Crystal structure: Orthorhombic

Space group: *Pna*2₁ (NO. 33)

Unit cell dimensions: $a = 6.824 \text{ \AA}$, $b = 8.346 \text{ \AA}$ and $c = 6.669 \text{ \AA}$

Atomic coordinates

Atom	Wyck	x/a	y/b	z/c
Ag	4a	0.409	0.128	0.113
Ga	4a	0.067	0.129	0.618
Se	4a	0.096	0.620	0.019
Se	4a	0.078	0.108	0.965

Note that the diffraction pattern was simulated starting from the orthorhombic AgInS₂ structure and substituting the In³⁺ and S²⁻ lattice positions with Ga³⁺ and Se²⁻ ions simultaneously. The unit cell diagrams of orthorhombic AgGaSe₂ NCs are shown in Fig. 1b in the manuscript.

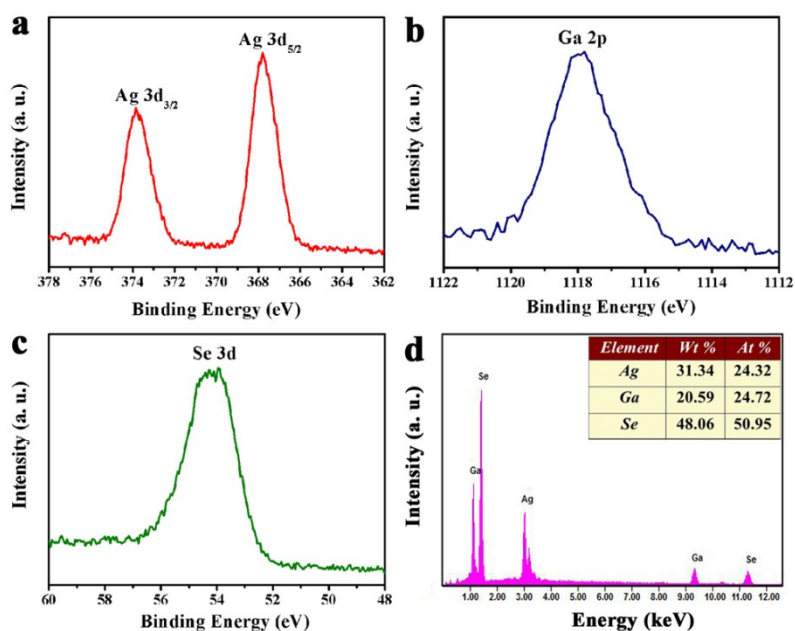


Fig. S1. XPS spectrum of the obtained AgGaSe₂ NCs: (a) Ag 3d, (b) Ga 2p, (c) Se 3d core levels. (d) Element composition of a field of AgGaSe₂ NCs measured by EDX.

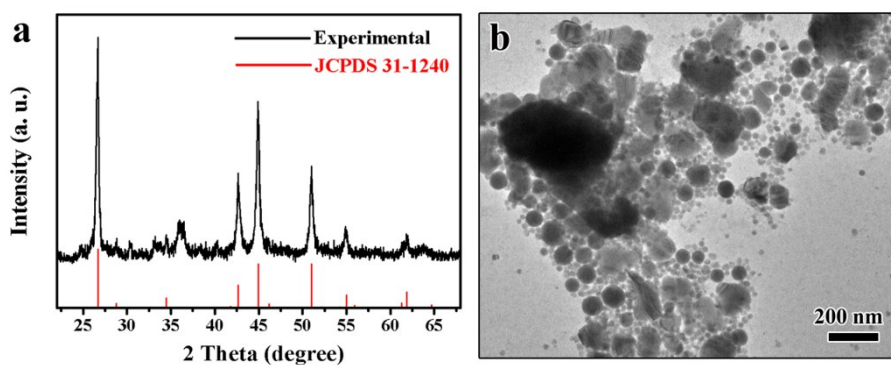


Fig. S2. (a) XRD pattern and (b) TEM image of the AgGaSe₂ NCs produced when 1 mL of OAm-Se and no oleylamine were presented in the reaction.

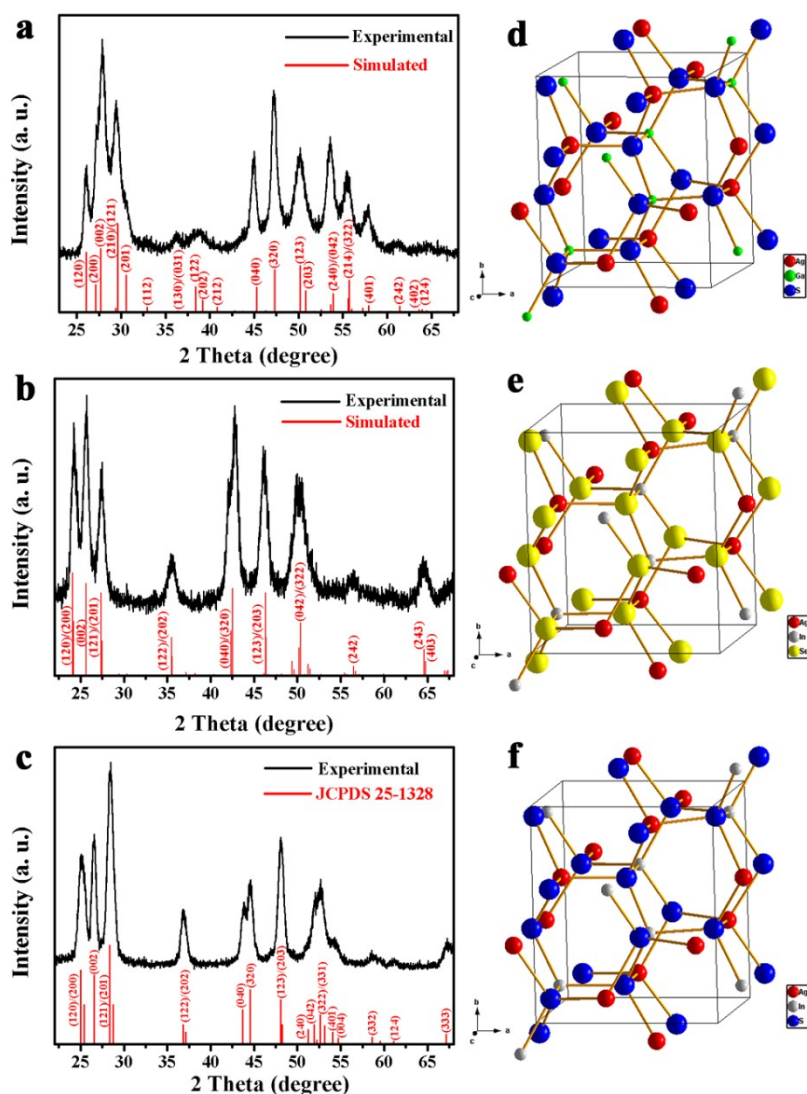


Fig. S3. The experimental and simulated powder XRD patterns (a)-(c), and the unit cell diagrams (d)-(f) of orthorhombic AgGaS₂, AgInSe₂ and AgInS₂ NCs, respectively.

Table S2. Comparison of experimental and simulated d-spacings for orthorhombic AgGaS₂ NCs

h	k	l	Simulated d-spacing (Å)	Experimental d-spacing (Å) ^a
1	2	0	3.416	3.415
2	0	0	3.282	
0	0	2	3.216	3.198
1	2	1	3.017	3.033
2	0	1	2.923	
1	1	2	2.716	
1	3	0	2.471	2.479
0	3	1	2.464	
1	2	2	2.341	2.322
2	0	2	2.297	
2	1	2	2.208	
0	4	0	2.000	2.018
3	2	0	1.920	1.924
1	2	3	1.816	1.815
2	0	3	1.795	
2	4	0	1.708	1.709
0	4	2	1.698	
3	2	2	1.648	1.653
4	0	1	1.590	1.591
2	4	2	1.509	1.513

^a d-spacing of all the distinct visible peaks from the XRD pattern.

Table S3. Comparison of experimental and simulated d-spacings for orthorhombic AgInSe₂ NCs

h	k	l	Simulated d-spacing (Å)	Experimental d-spacing (Å) ^a
1	2	0	3.688	
2	0	0	3.672	3.671
0	0	2	3.468	3.470
1	2	1	3.256	3.257
2	0	1	3.245	
1	2	2	2.526	2.525
2	0	2	2.521	
0	4	0	2.133	
3	2	0	2.123	2.112

1	2	3	1.959	1.967
2	0	3	1.956	
2	4	0	1.844	
0	4	2	1.817	1.826
3	2	2	1.811	1.806
2	4	1	1.782	1.775
4	0	1	1.775	
2	4	2	1.628	1.630
2	4	3	1.442	1.442
4	0	3	1.438	

^a d-spacing of all the distinct visible peaks from the XRD pattern.

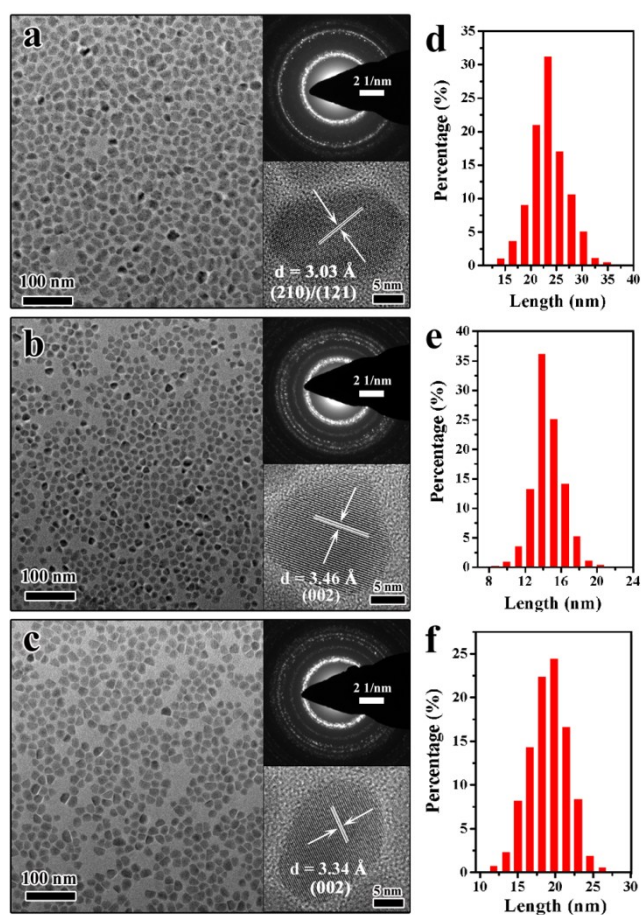


Fig. S4 (a)-(c) TEM images of AgGaS₂, AgInSe₂ and AgInS₂ NCs. The insets show the corresponding SAED patterns and HRTEM images. (d)-(f) Size distribution of the AgGaS₂, AgInSe₂ and AgInS₂ NCs determined by (a)-(c) respectively.

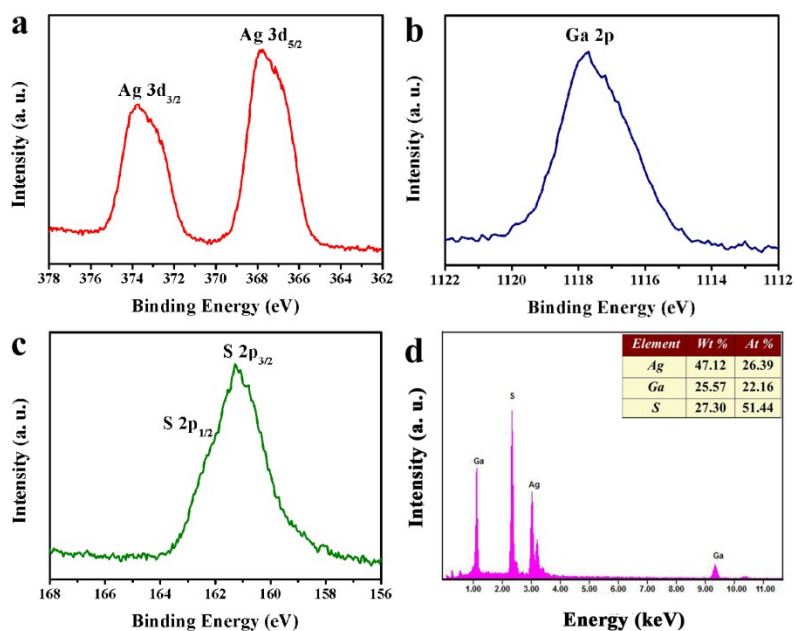


Fig. S5. XPS spectrum of the obtained AgGaS₂ NCs: (a) Ag 3d, (b) Ga 2p, (c) S 2p core levels. (d) Element composition of a field of AgGaS₂ NCs measured by EDX.

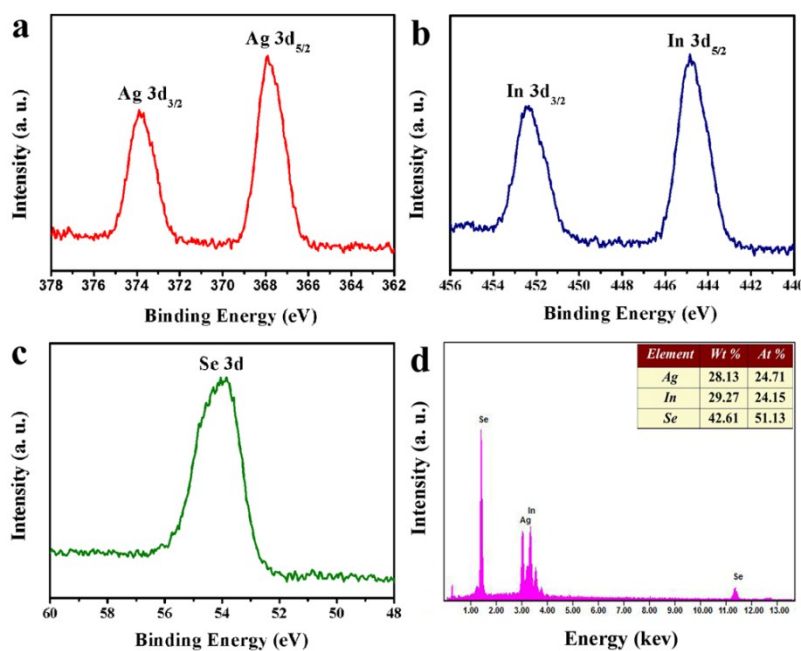


Fig. S6. XPS spectrum of the obtained AgInSe₂ NCs: (a) Ag 3d, (b) In 3d, (c) Se 3d core levels. (d) Element composition of a field of AgInSe₂ NCs measured by EDX.

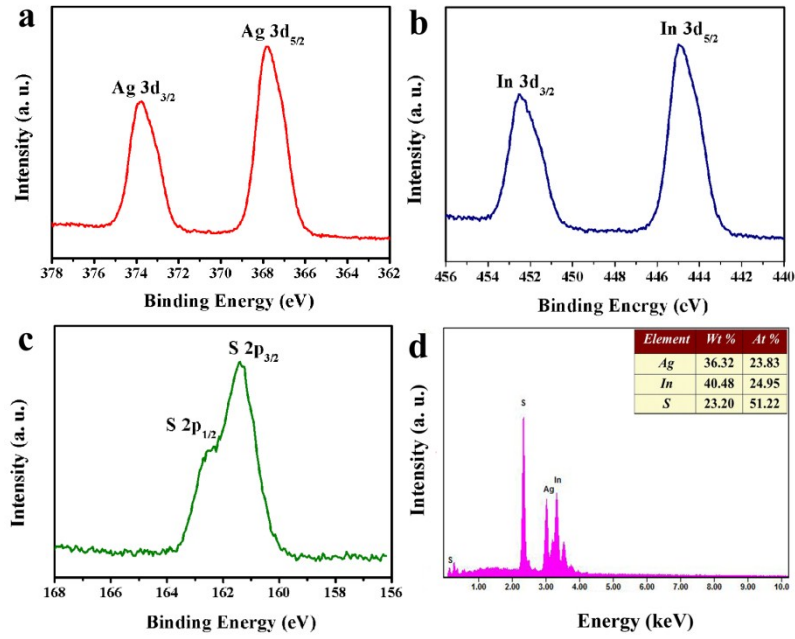


Fig. S7. XPS spectrum of the obtained AgInS_2 NCs: (a) Ag 3d, (b) In 3d, (c) S 2p core levels. (d) Element composition of a field of AgInS_2 NCs measured by EDX.

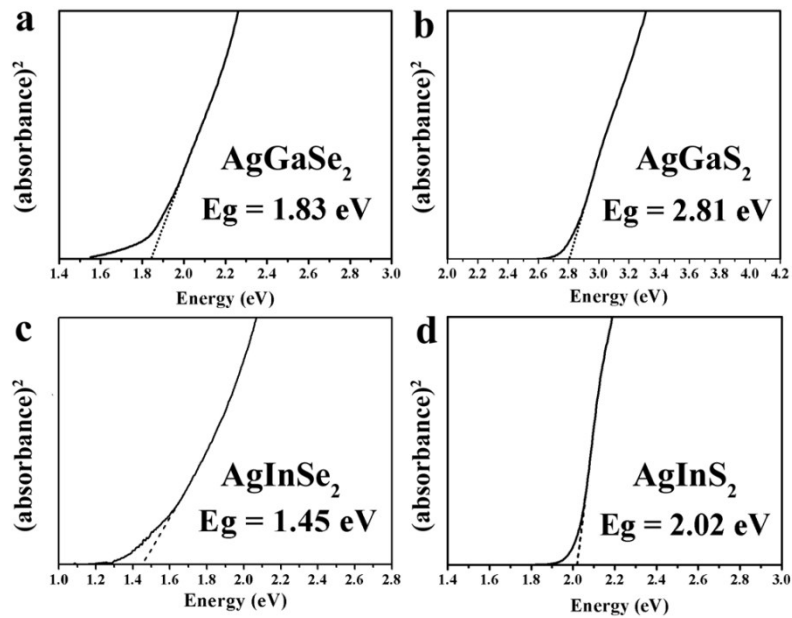


Fig. S8. The optical band gaps of (a) AgGaSe_2 , (b) AgGaS_2 , (c) AgInSe_2 and (d) AgInS_2 NCs are approximated by plotting the absorbance squared versus energy, and extrapolating to zero.