Supplementary Information

Cation-exchange and lateral ripening in wurtzite-like $CuInSe_2$ formation from weissite-like $Cu_{2-x}Se$

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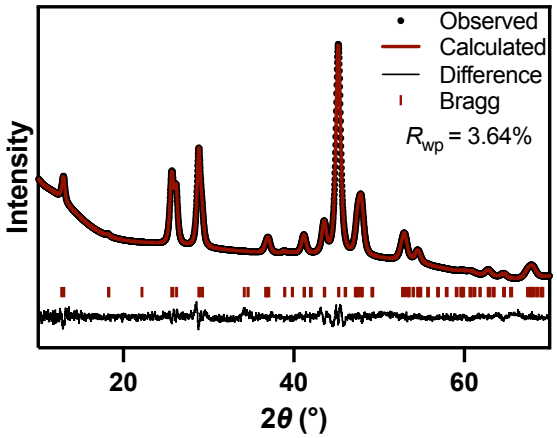

Fig. S1 Rietveld refinement of the weissite-like $Cu_{2-x}Se$ XRD pattern using the $Cu_{2-x}Te$ structural model (space group $P\bar{3}m1$). Experimental data were collected with λ = 1.5406 Å. Reference peaks and refinement quality indicators are shown.[1,2]

Table S1. Crystal structure parameters of weissite-like $Cu_{2-x}Se$ obtained by Rietveld refinement using the trigonal $Cu_{2-x}Te$ structural model (space group $P\bar{3}m1$, No. 164).[3] Lattice parameters are: $a = b = 8.016(1)$ Å, $c = 6.794(2)$ Å.

Atom	x/a	y/b	z/c
Cu	0.3333	0.6667	0.0725(56)
Cu	0.0000	0.0000	0.2800
Cu	0.4838(10)	0.5162	0.3156(25)
Cu	0.8267(14)	0.1733	0.4148(31)

Se	0.1600(13)	0.8400	0.2281(19)
Se	0.3333	0.6667	0.81(81)

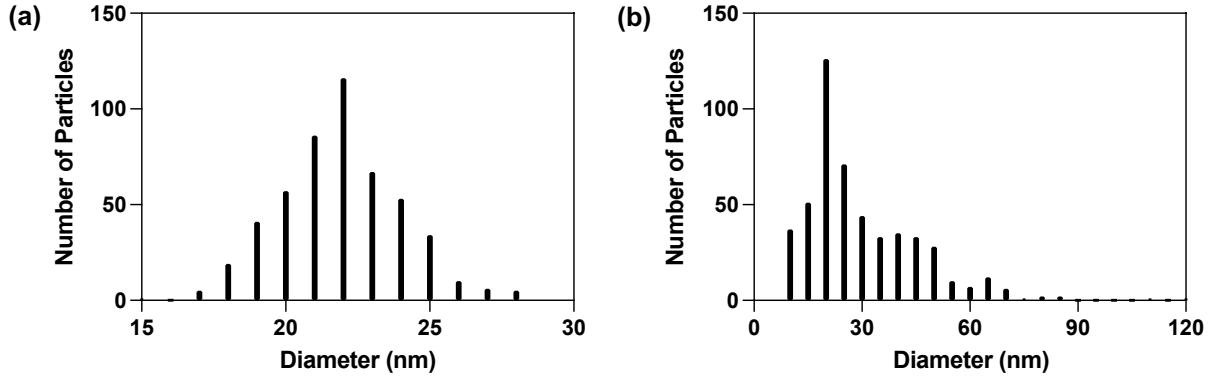

Fig. S2 Size distributions of isolated nanocrystals from reactions where no aliquots were withdrawn. (a) Weissite-like $Cu_{2-x}Se$, showing a narrow distribution with an average diameter of 21.9 ± 2.1 nm (N = 500), indicative of monodisperse nanoplates. (b) Wurtzite-like $CuInSe_2$, showing a broader distribution with an average diameter of 30.1 ± 16.0 nm (N = 500), reflecting lateral growth and size broadening during cation exchange.

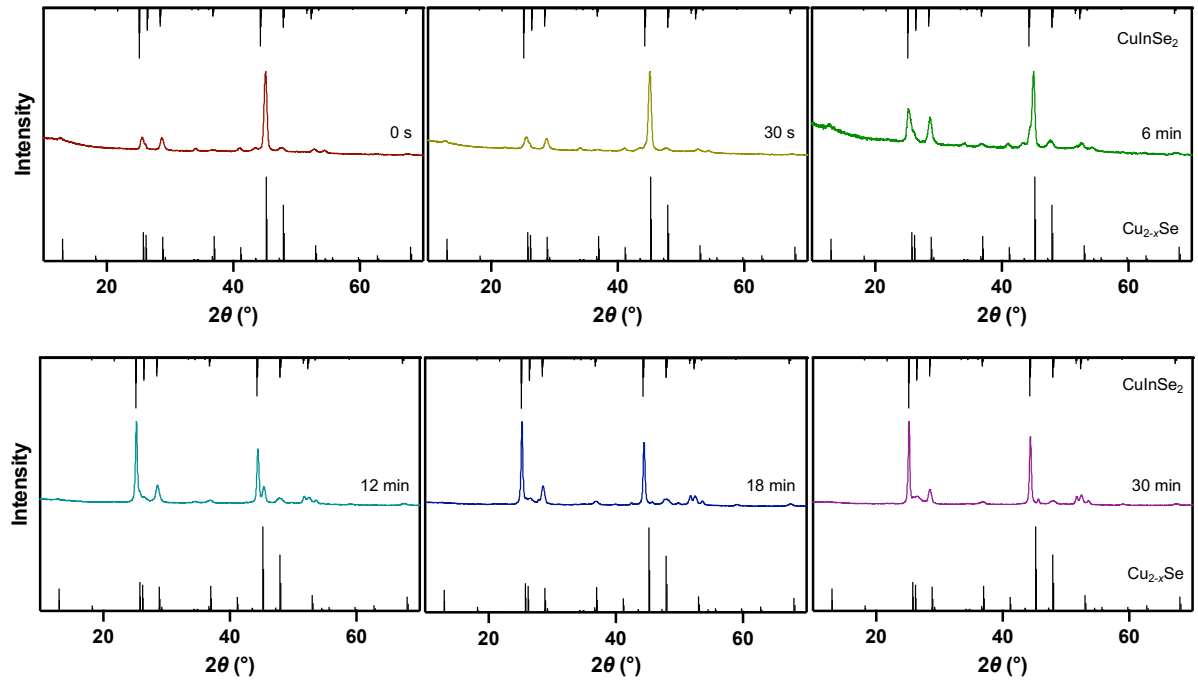

Fig. S3 Individual powder XRD patterns from Fig. 2a, showing steady structural evolution from weissite-like $Cu_{2-x}Se$ to wurtzite-like $CuInSe_2$.

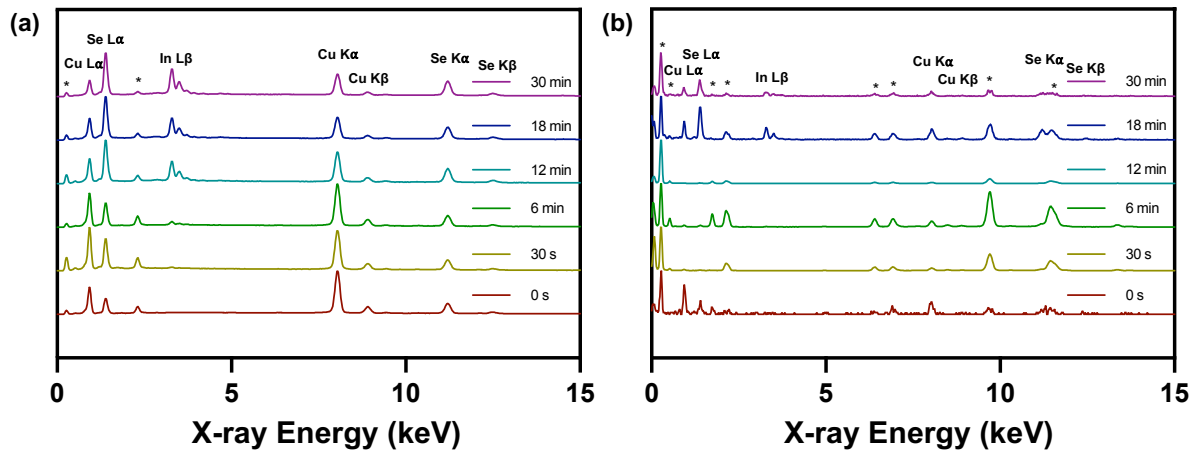

Fig. S4 EDX spectra showing steady indium incorporation over time. (a) SEM-EDX spectral data for aliquots taken from 0 s to 30 min. (b) STEM-EDX spectral data for aliquots taken from 0 s to 30 min. "*" consists of impurities coming from carbon tabs, Au TEM grids, or the TEM holder (C, Fe, S, Co, Au).

Table S2. Quantitative SEM-EDX elemental compositions of aliquots collected during the cation exchange reaction from weissite-like $Cu_{2-x}Se$ to wurtzite-like $CuInSe_2$ (Fig. 2b). Values represent mean atomic percentages with standard deviations given in parentheses.

Aliquot	Cu at. %	In at. %	Se at. %
0 s	61.6(8)	0	38.4(8)
30 s	59.3(8)	1.2(2)	39.6(8)
6 min	59.4(7)	3.1(1)	37.6(6)
12 min	40.4(9)	16.9(9)	42.7(8)
18 min	34.5(3)	20.9(5)	44.5(6)
30 min	29.7(6)	23.0(12)	47.3(9)

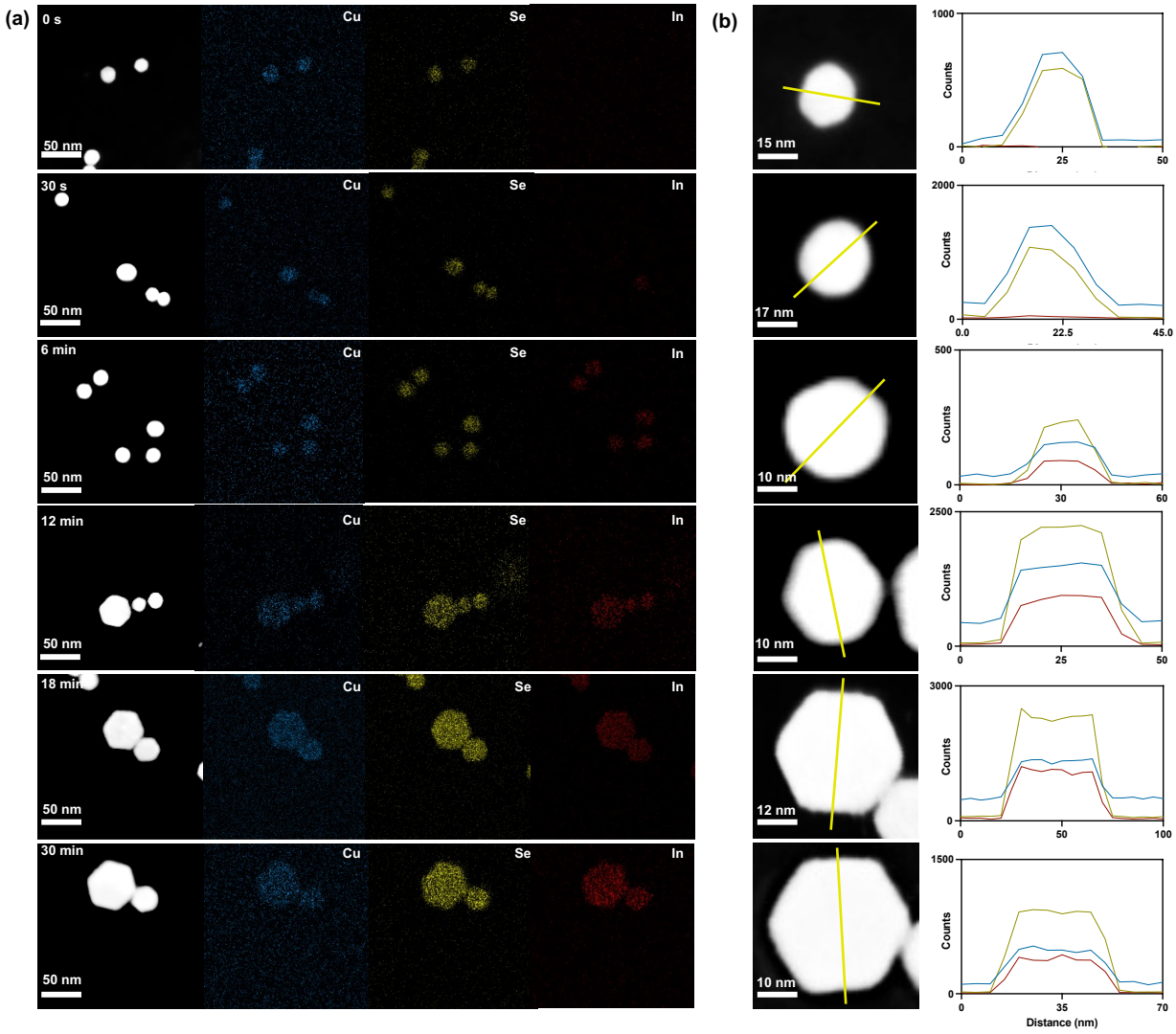

Fig. S5 STEM-EDX elemental mapping of the transformation from weissite-like $Cu_{2-x}Se$ to wurtzite-like $CuInSe_2$ during a time-resolved aliquot study. (a) Aliquots were collected at 0 s, 30 s, 6 min, 12 min, 18 min, and 30 min, showing the spatial and compositional evolution of the nanocrystals. Indium incorporation proceeds isotropically across the nanocrystals over time, with minor incorporation starting at 30 s. (b) Line scan analysis emphasizing uniformity across the nanoplate diameter. *K* lines were used for Cu and *L* lines were used for Se and In.

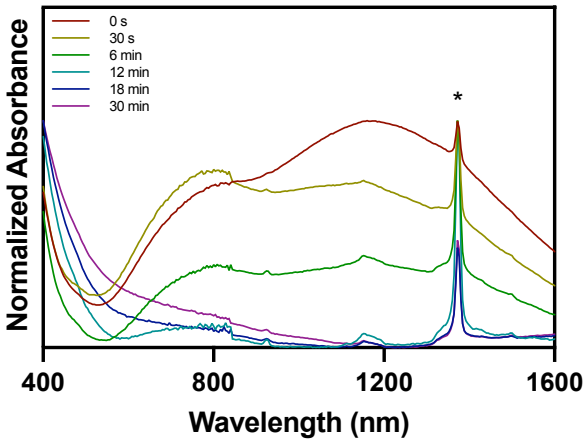

Fig. S6 UV–vis–NIR absorption spectra of aliquots collected during the reaction. The localized surface plasmon resonance of weissite-like $Cu_{2-x}Se$ diminishes over time, while band edge features characteristic of wurtzite-like $CuInSe_2$ emerge.

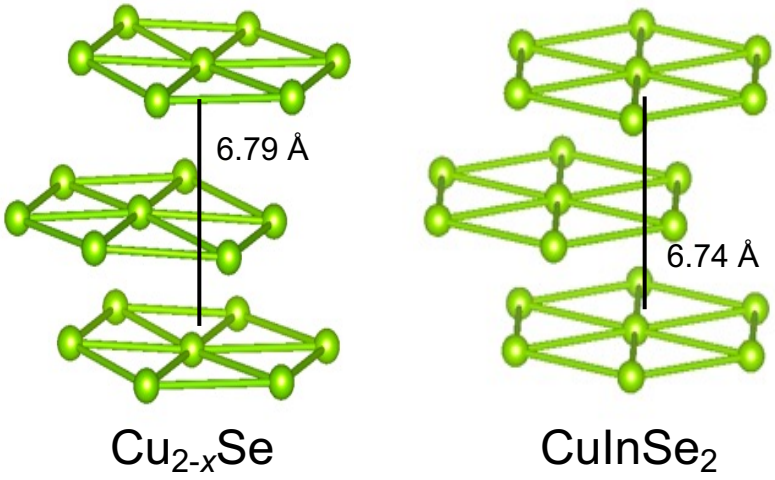

Fig. S7 Hexagonally close-packed (HCP) anion sublattices of weissite-like $Cu_{2-x}Se$ and wurtzite-like $CuInSe_2$. The interlayer spacing differs by 0.05 Å between every other layer. Distances were determined using VESTA.

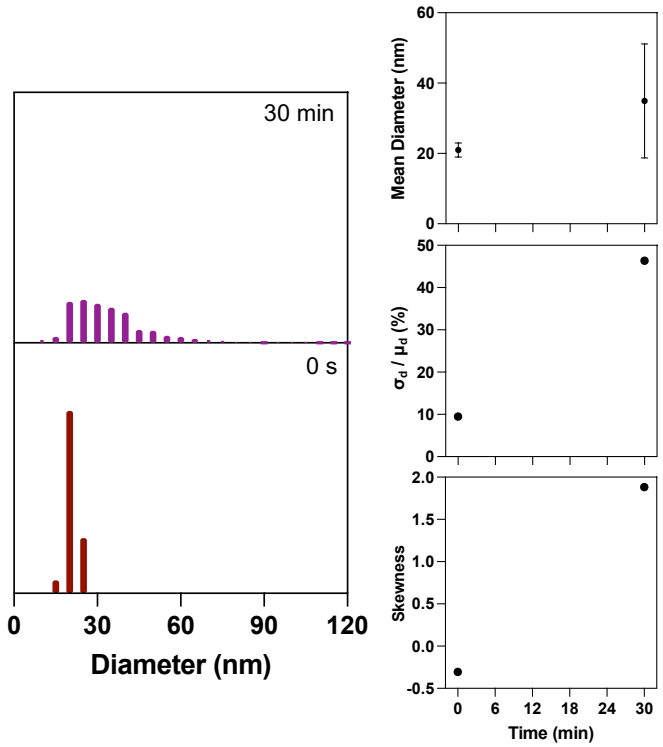

Fig. S8 Size analysis study of aliquots taken at 0 s and 30 min time points of an independent synthesis performed identically to demonstrate reproducibility. Size distribution analyses are consistent with each other, showing average particle diameters of 21.0 ± 2.0 nm and 34.9 ± 16.2 nm for $Cu_{2-x}Se$ and $CuInSe_2$, respectively. The particle size skew increases from -0.31 to 1.88, further enforcing reproducibility.

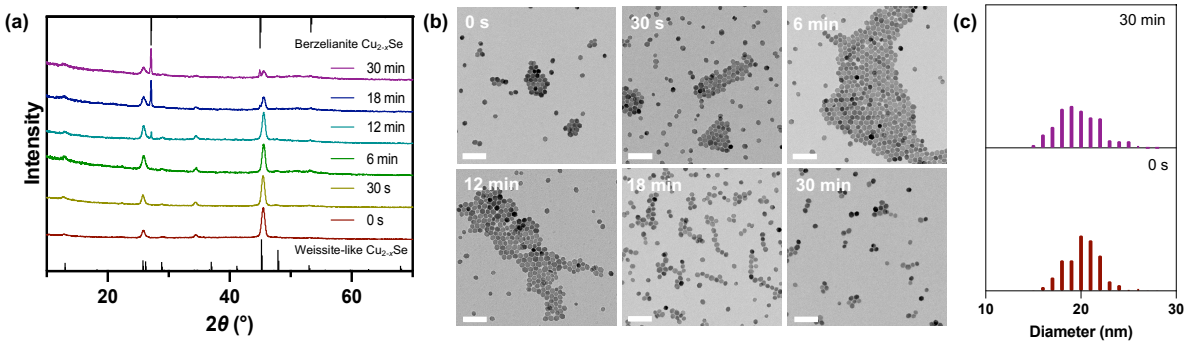

Fig. S9 (a) Aliquot study showing the structural evolution of weissite-like $Cu_{2-x}Se$ over time in the absence of an indium source. The top stick pattern corresponds to berzelianite $Cu_{2-x}Se$ (ICSD Coll. Code: 41143). (b) TEM images showing the hexagonal plate morphology over time; all scale bars = 100 nm. (c) Size distribution of aliquots taken at 0 s and 30 min, showing narrow distribution with average sizes of 20.2 ± 1.8 nm and 19.7 ± 2.2 nm, respectively, indicative of monodisperse nanoplates.

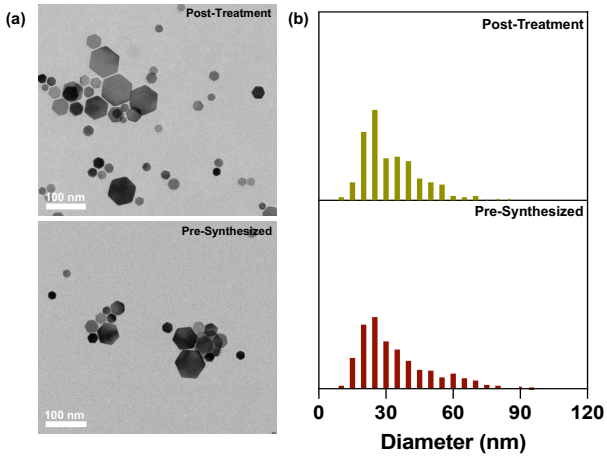

Fig. S10 Control experiment to assess ripening of the product phase in the absence of soluble precursors. (a) TEM images of pre-synthesized $CuInSe_2$ nanocrystals before and after re-dispersion in neat oleylamine and heat treatment under the standard cation-exchange protocol, confirming retention of the hexagonal nanoplate morphology. (b) Size distributions (N = 500) before and after treatment, with mean lateral sizes of 34.2 ± 16.4 nm and 32.2 ± 13.1 nm, respectively.

References

1. N. Doebelin and R. Kleeberg, *J. Appl. Crystallogr.*, 2015, **48**, 1573–1580.
2. R. A. Young, Ed., *The Rietveld Method*, Oxford University PressOxford, 1993.
3. L. Yu, K. Luo, S. Chen and C.-G. Duan, *CrystEngComm*, 2015, **17**, 2878–2885.