Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for:

Anion Exchange Induced Formation of Kesterite Copper Zinc Tin Sulphide-Copper Zinc Tin Selenide Nanoheterostructures

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This supporting information includes:
Figure S1-S14;
References

Table S1. EDS results of CZTSSe nanocrystals.

Control Experiments		Ref.	Cu (%)	Zn(%)	Sn(%)	S(%)	Se(%)
CZTS		Figure 1a-c	27.1	10.4	14.2	48.3	N.A.
Injection of Se-precursor	30 sec	Figure S14a-b	27.5	9.5	14.1	47.0	1.9
	2 min	Figure S14c-d	26.8	9.4	10.6	50.1	3.1
	5 min	Figure S14e-f	28.1	9.9	12.9	44.1	5.0
	10 min	Figure S14g-h	27.7	9.7	13.8	39.9	8.9
CZTS-CZTSe		Figure 3	28.9	9.1	14.3	35.7	12.0

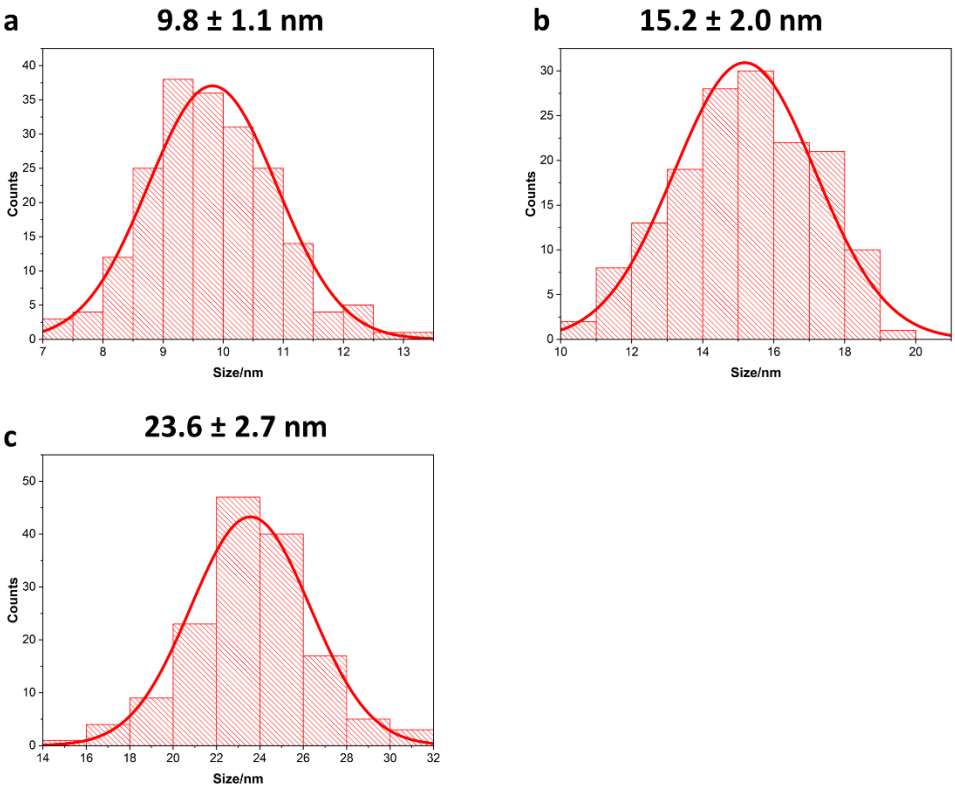

Figure S1. Size distribution histogram of (a) kesterite CZTS NCs, (b) short and (c) long axis of ellipsoidal CZTS-CZTSe heterostructures.

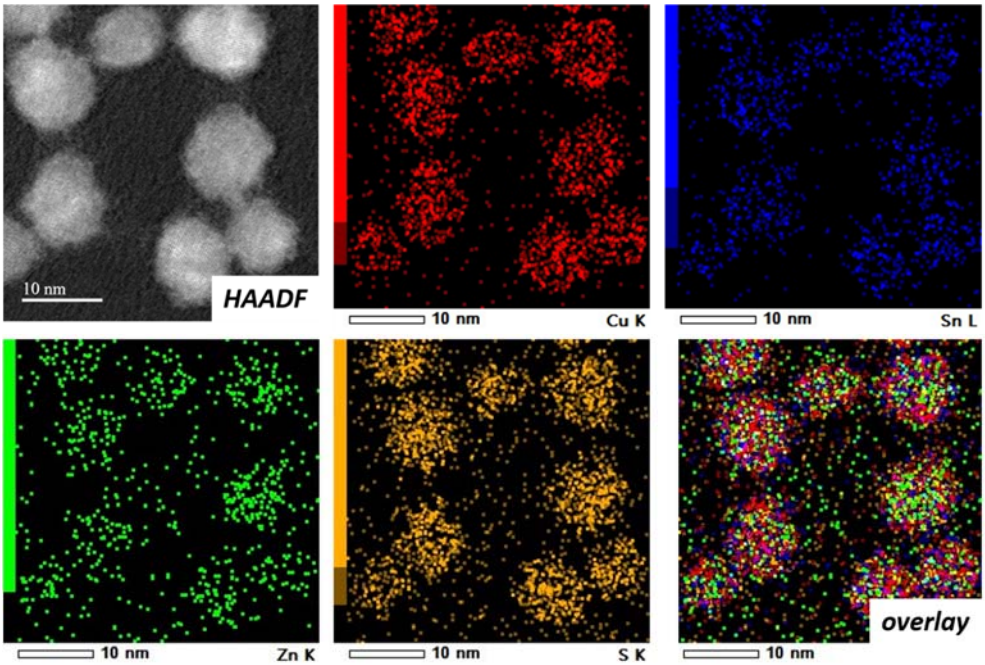

Figure S2. Additional STEM-EDS maps of Cu, Sn, Zn, and S for CZTS NCs.

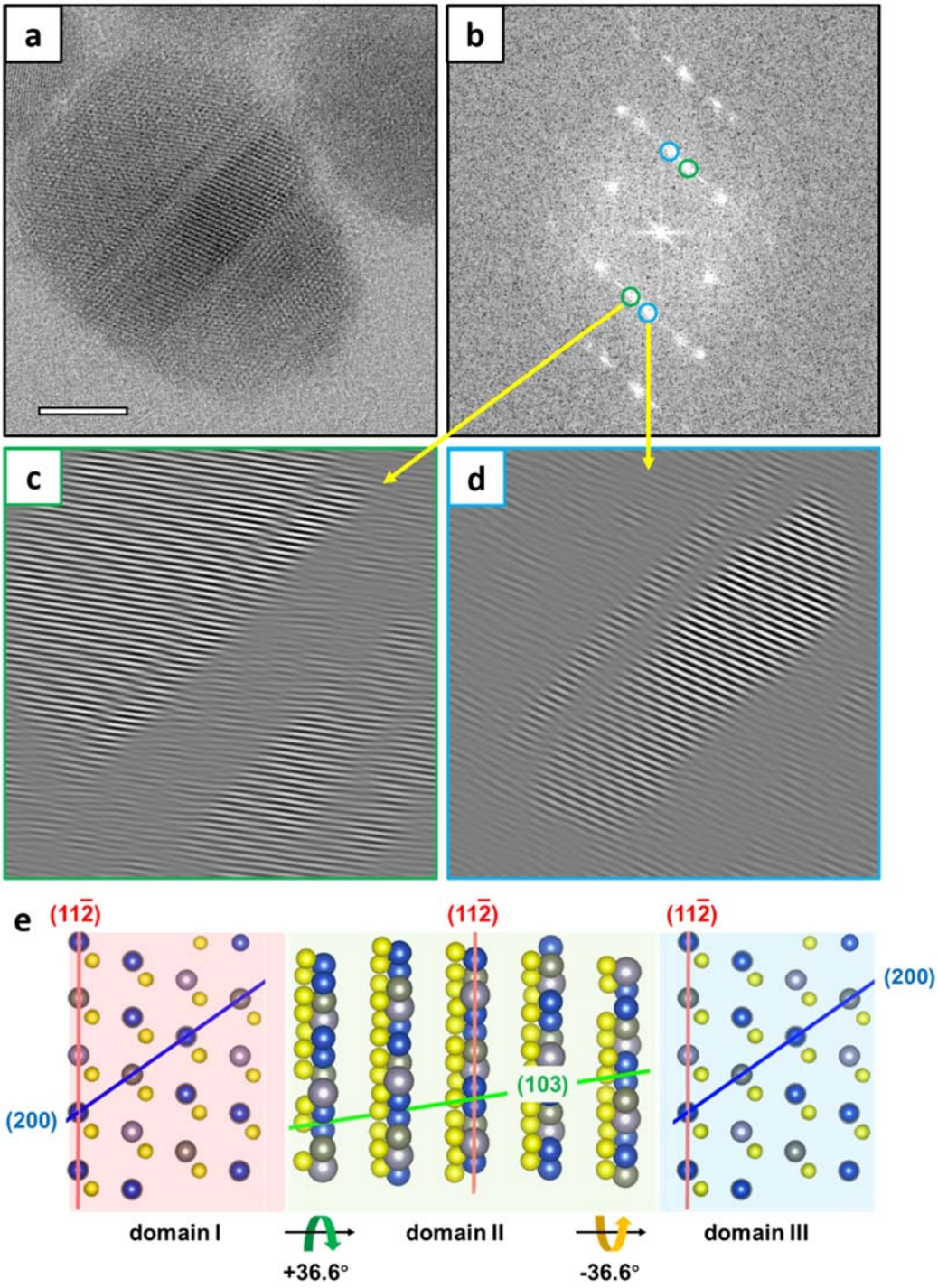

Figure S3. (a) HRTEM image and (b) corresponding FFT pattern of a triple domain CZTS NC (the same one shown in Fig. 1(c). (c-d) FFT filter analysis indicate the green FFT spots is generated from the lattices from I and III domain, the periodicity of lattice in center domain generates the blue FFT spots. (e) A schematic illustration shows the crystallographic relationship between three domains.

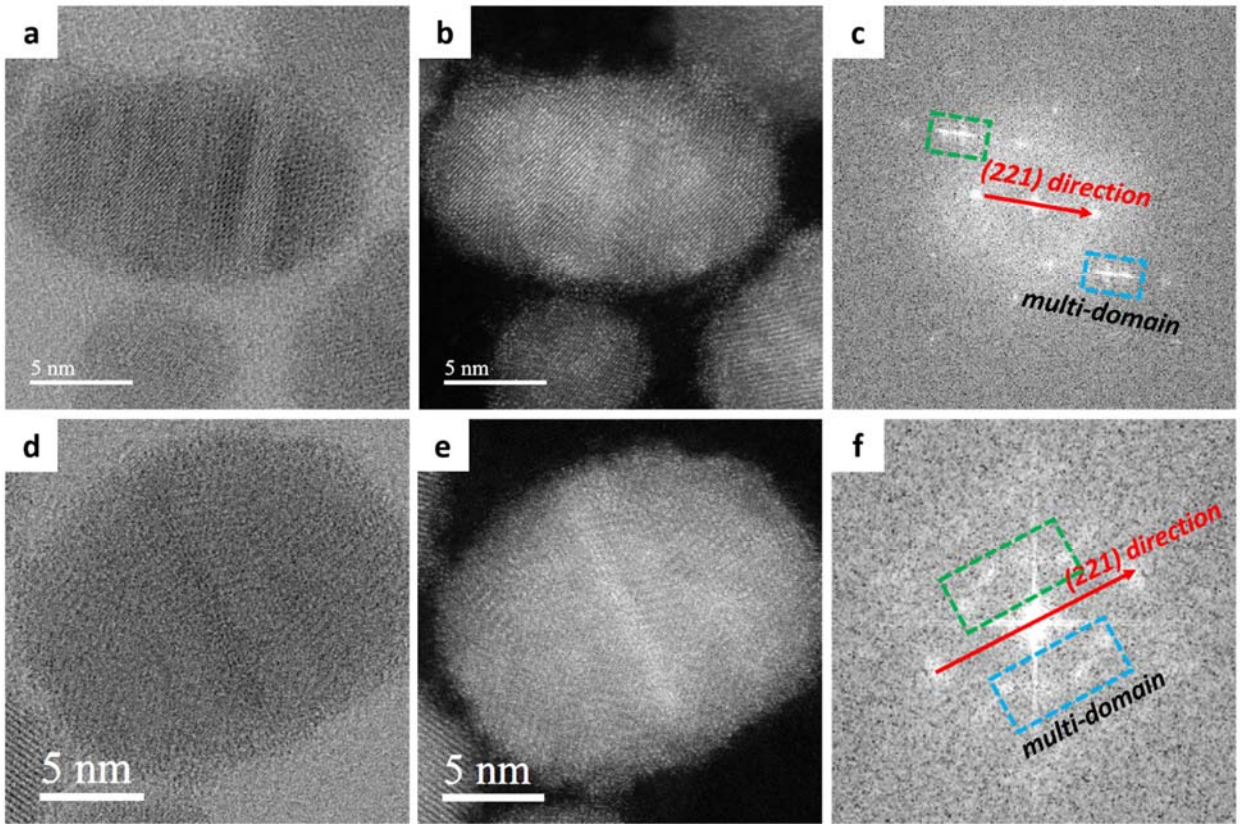

Figure S4. Additional example of multi-domain CZTS NCs. (a,d) HRTEM and (b,e) STEM images of multi-domain CZTS NCs. Panels (c,f) are corresponding FFT patterns of (b,e).

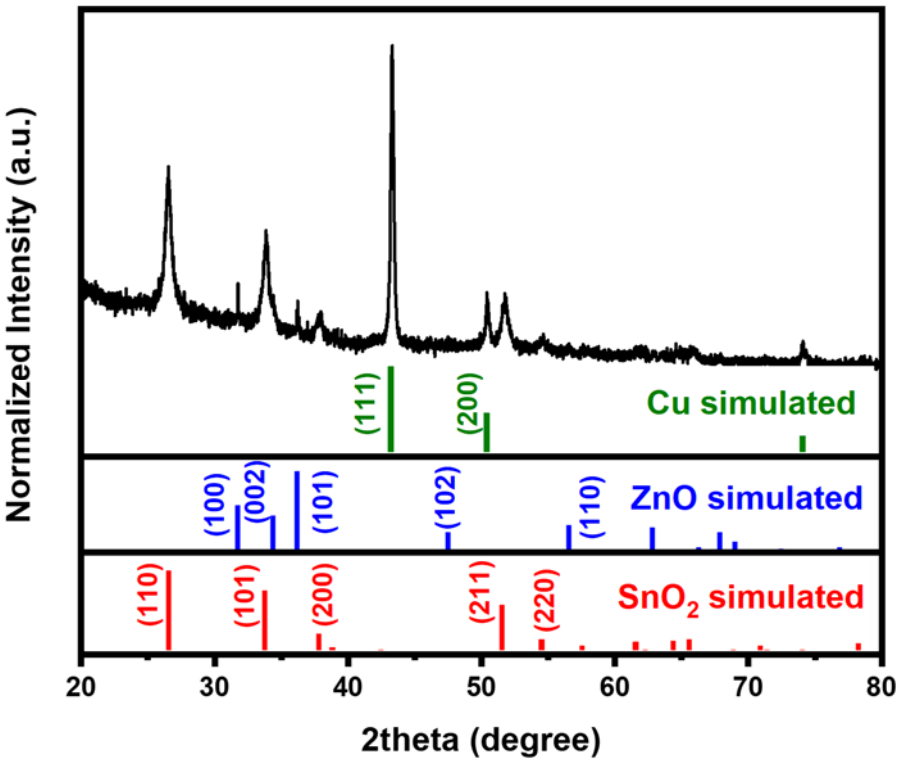

Figure S5. XRD pattern from products in an aliquot taken from the reaction precursors heated to 225 °C (before sulfur precursor injection).

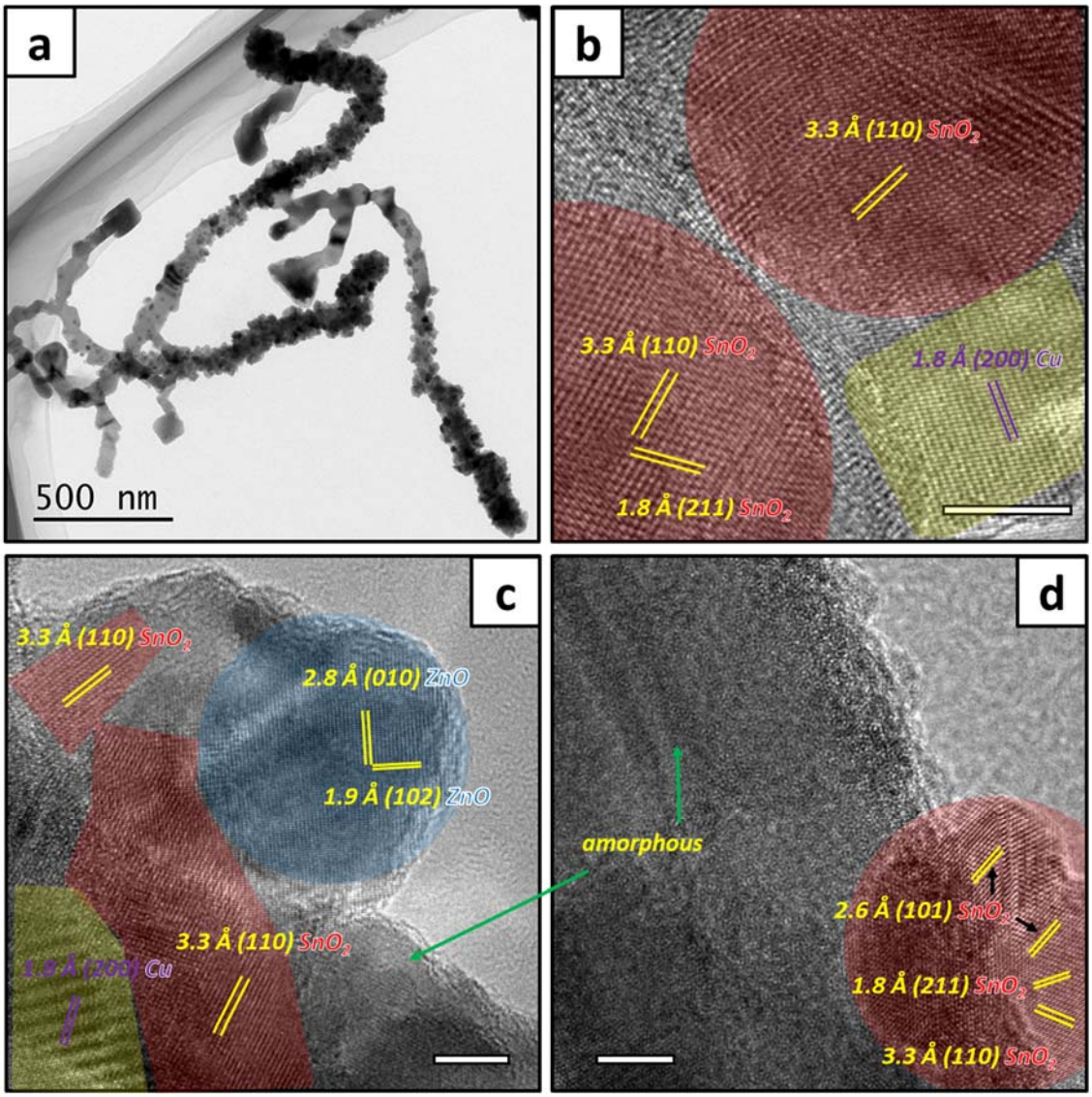

Figure S6. TEM and HRTEM images of products in an aliquot extracted from reaction precursors heated to 225 °C, (before sulfur precursor injection). These images and the XRD of Fig. S5 show the presence of Cu, SnO_2 and ZnO along with amorphous material. The scale bars in panels (b-d) are all 5 nm.

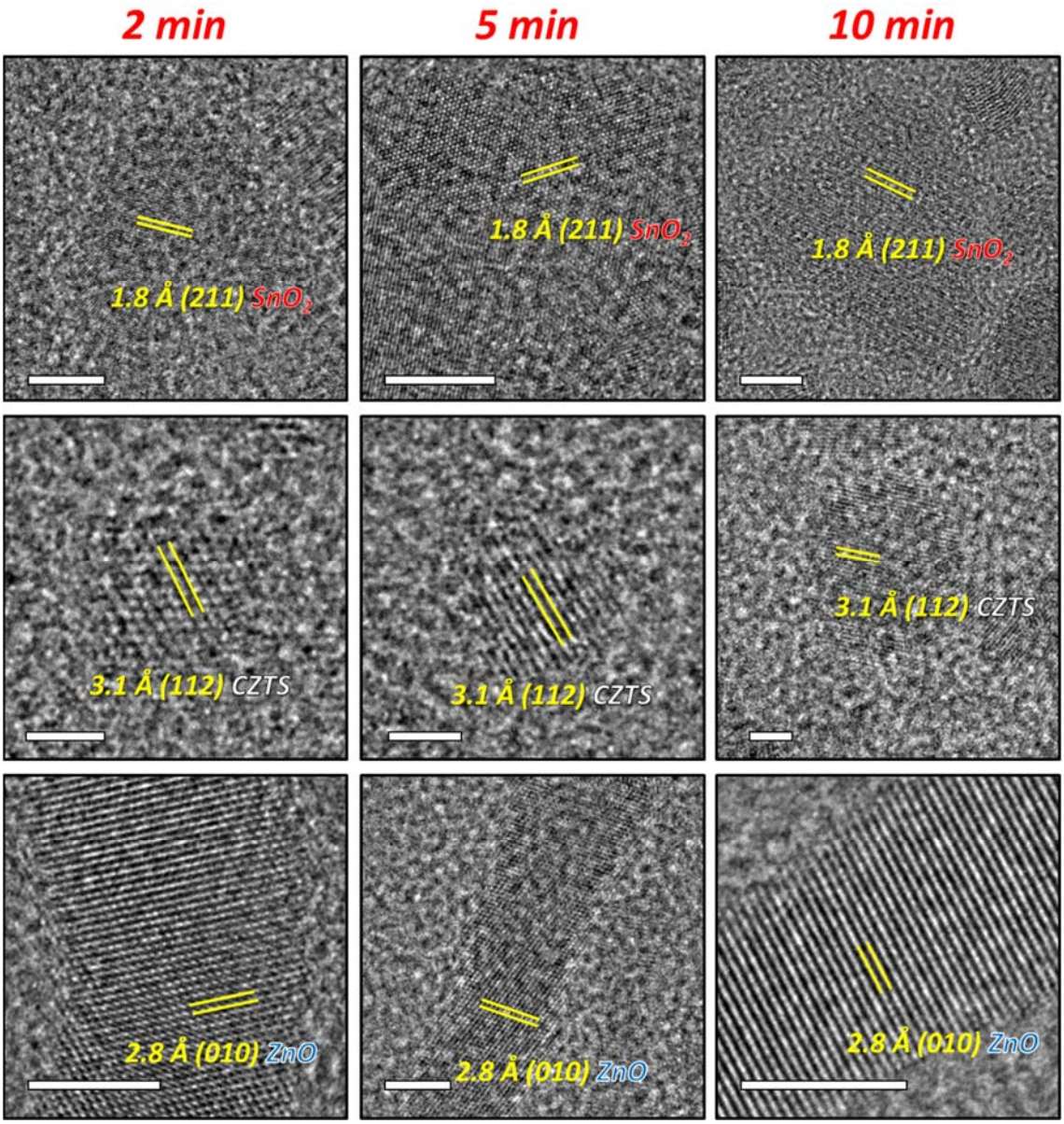

Figure S7. HRTEM images of reaction intermediates obtained in aliquots extracted 2, 5, and 10 min after S-precursor injection (each column). The scale bars in panels containing SnO_2 and CZTS particles are 2 nm, and those in panels containing ZnO particles are 5 nm.

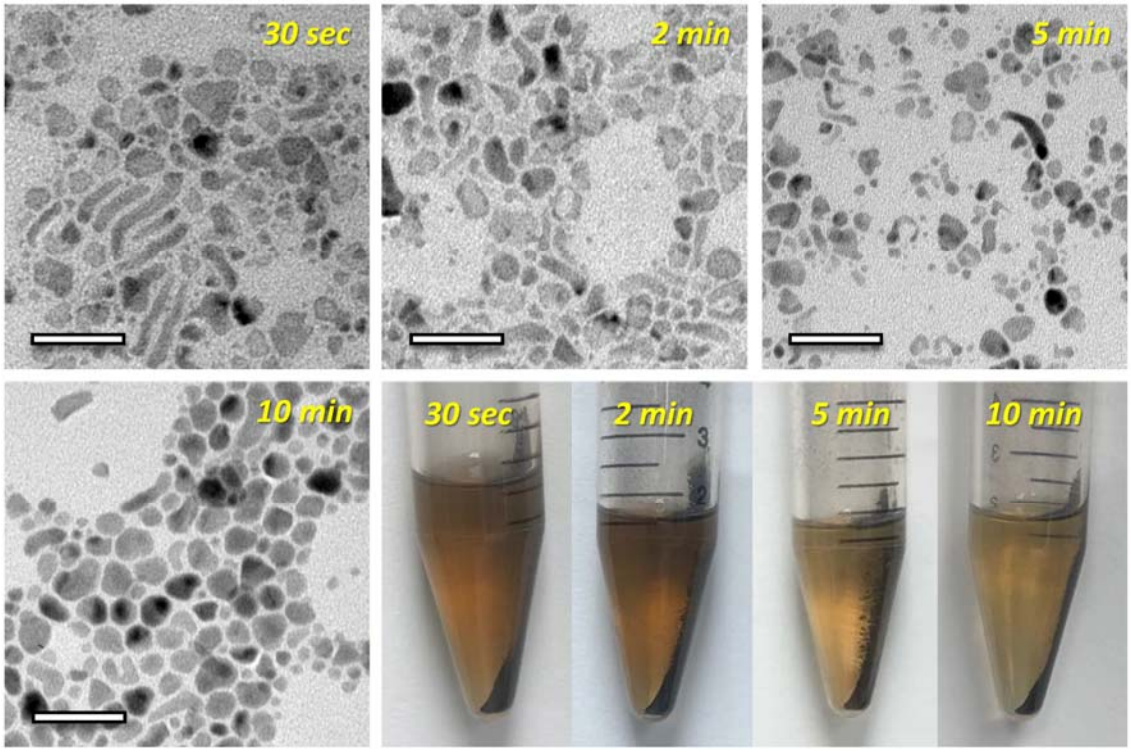

Figure S8. TEM images of reaction intermediates obtained from aliquots extracted 30 sec, 2, 5, and 10 min after S-precursor injection. Photographs showing supernatant of these aliquots after centrifugation. The color of supernatant becomes lighter as the reaction proceeds, indicating a decrease in the concentration of small NCs in the supernatant, consistent with the observations in TEM imaging. The scale bars in all TEM micrographs are 50 nm.

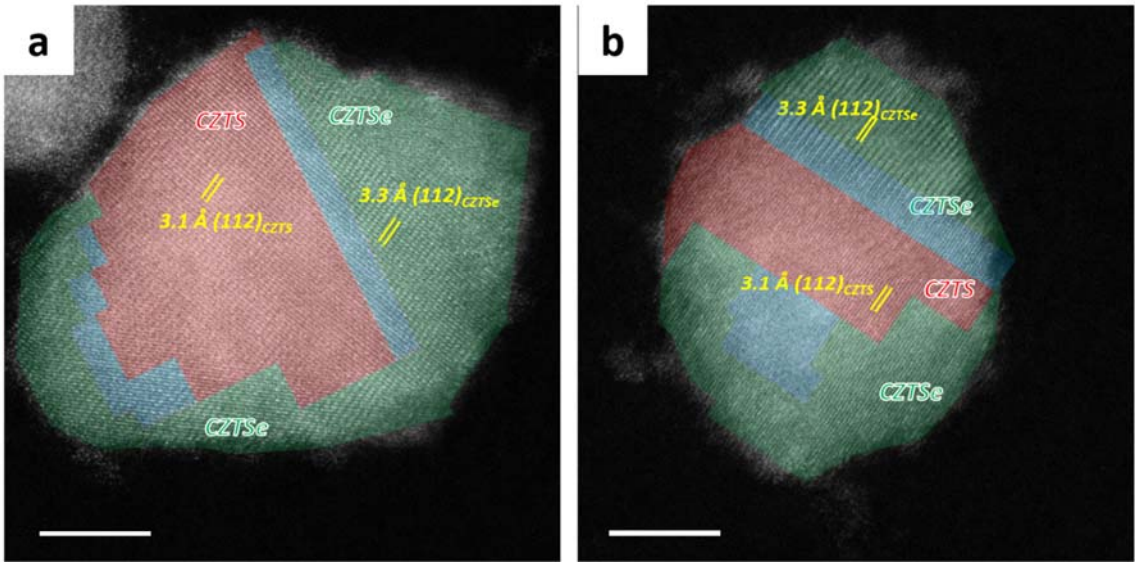

Figure S9. Additional HRSTEM images of more examples of CZTS-CZTSe heterostructures. The red, green and blue regions are CZTS, CZTSe and diffusion layer, respectively. The scale bars are 5 nm.

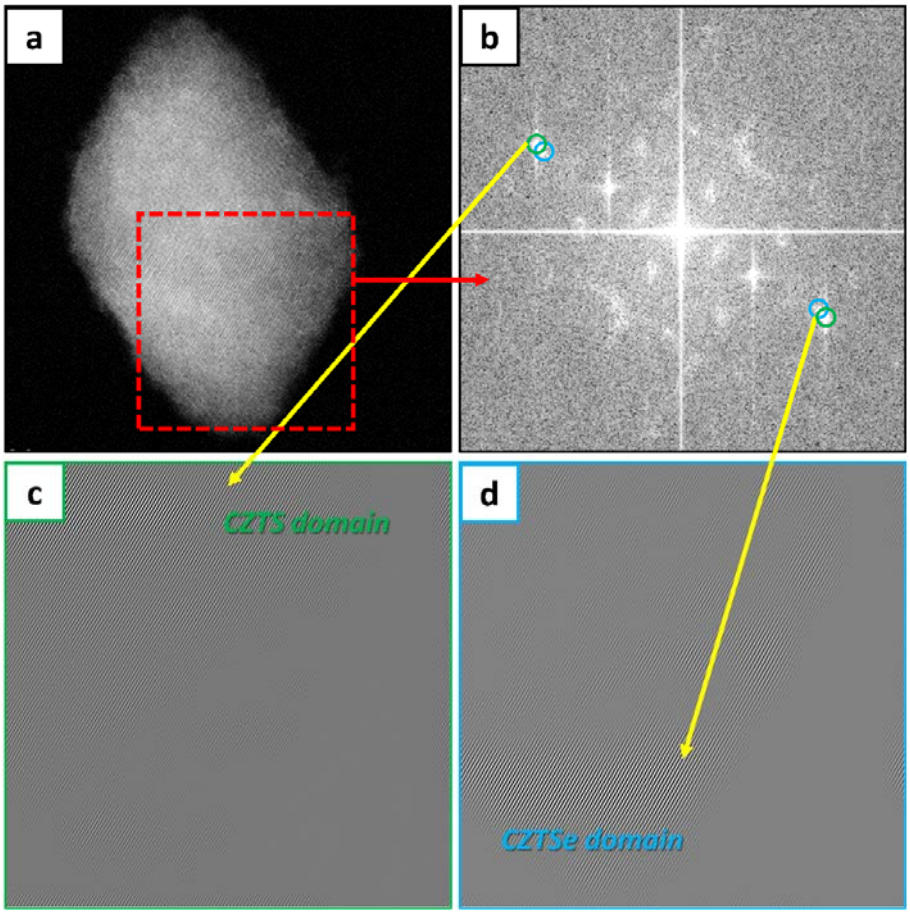

Figure S10. (a) HRTEM image and (b) corresponding FFT pattern of a CZTS-CZTSe NC (the one shown in Figure 3c). (c-d) FFT filter analysis indicating that the green FFT spots are generated by the lattices from CZTS domain with smaller lattice spacing, while the CZTSe domains generate the blue FFT spots.

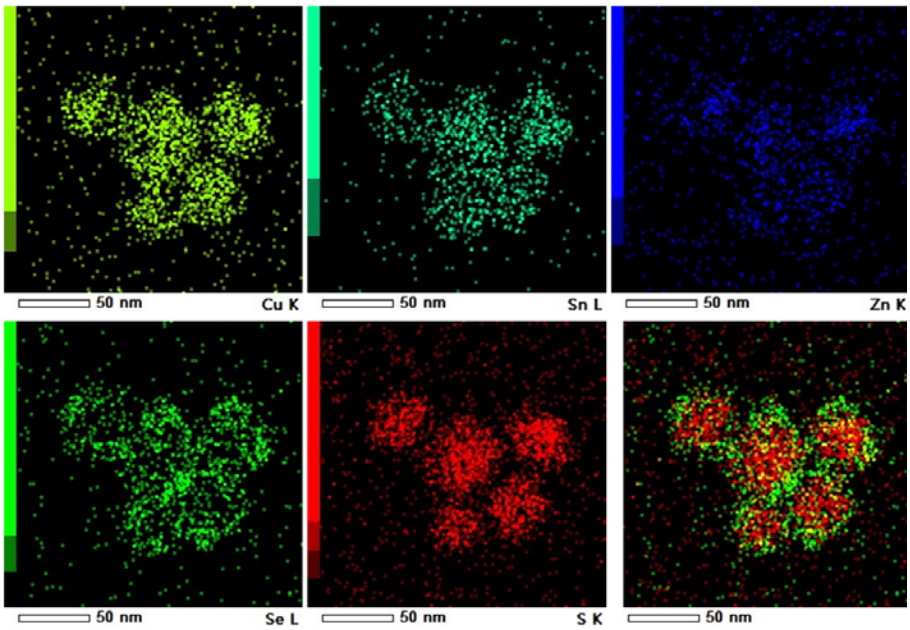

Figure S11. Additional STEM-EDS maps of Cu, Sn, Zn, Se, and S for CZTS-CZTSe NCs.

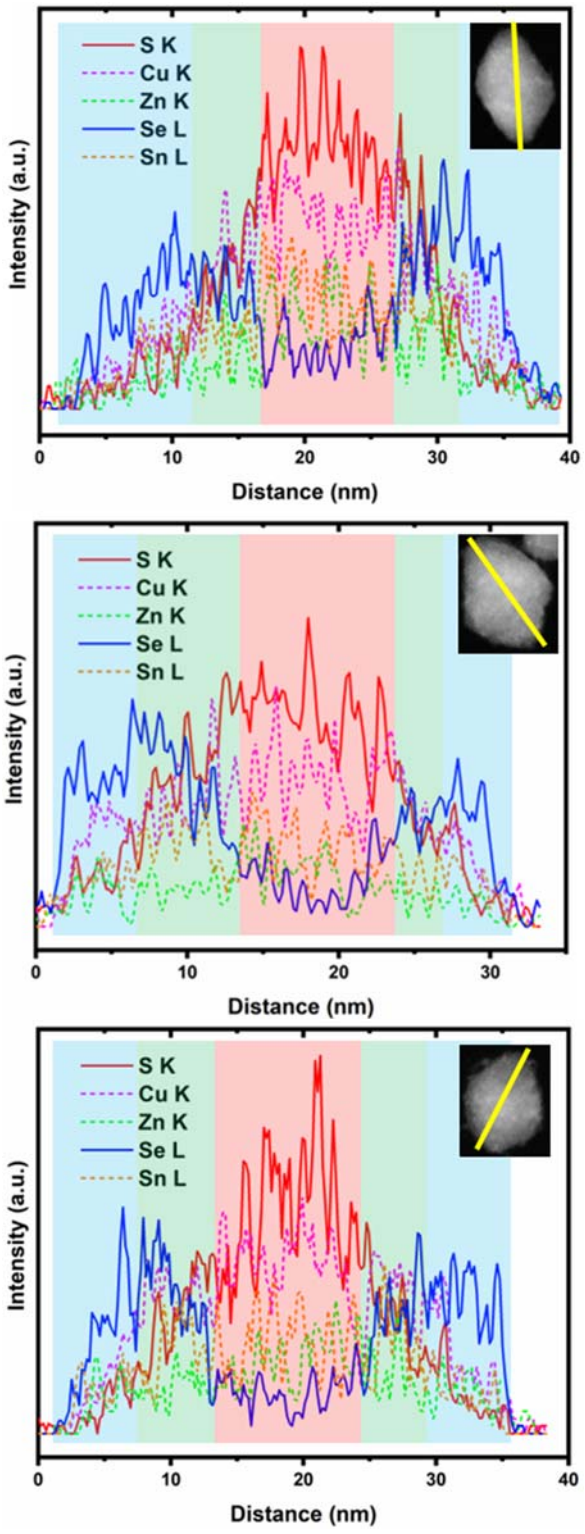

Figure S12. STEM-EDS line scans of CZTS-CZTSe heterostructures. For clarity, we use dashed lines to present Cu, Zn, and Sn signals, while solid lines are represented S and Se. Regions of different domains are shaded with different colors: CZTS (red), CZTSSe (green), CZTSe (blue). The insets show the line measured for each line scan.

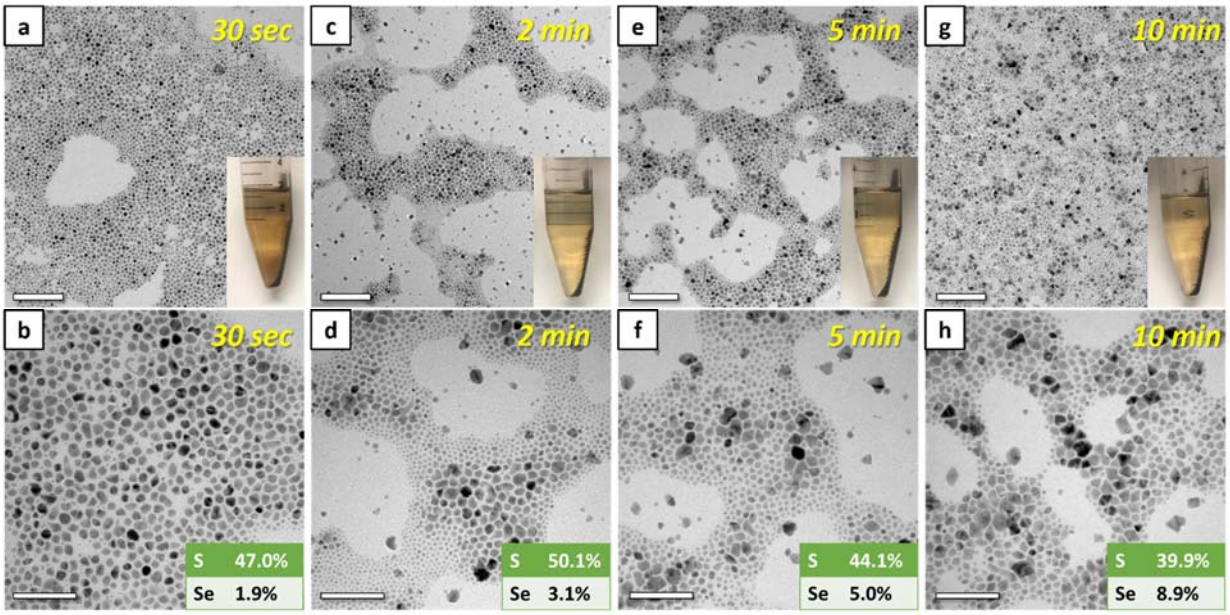

Figure S13. TEM images of products obtained in aliquots extracted 30 sec, 2, 5, and 10 min after Se-precursor injection. Photographs of the supernatant after centrifugation are shown as insets. The color of supernatant faded as the reaction proceeded, indicating consumption of precursors. The scale bars in lower magnification panels (top row) and in higher magnification panel (bottom row) are 200 and 50 nm, respectively.

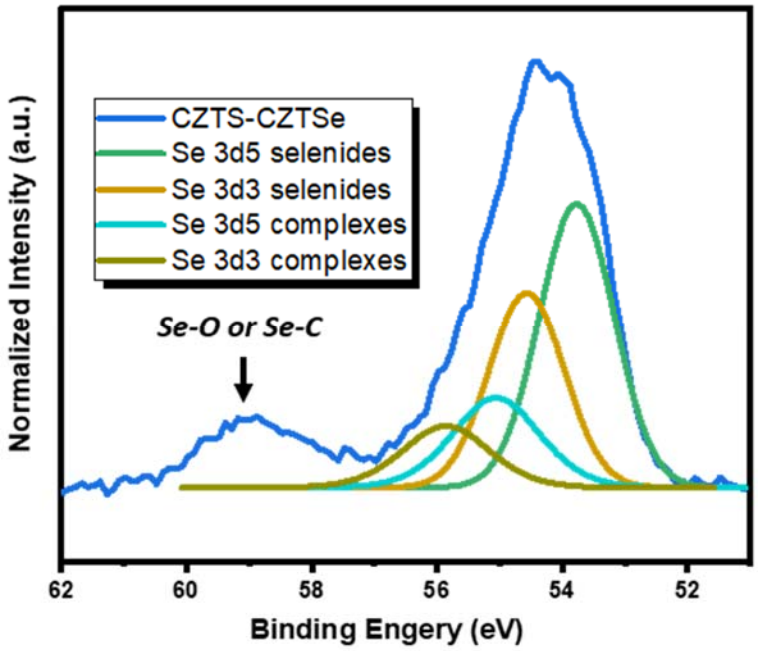

Figure S14. High-resolution XPS spectra of Se 3*d* region for CZTS-CZTSe heterostructures. The peak with a binding energy of ~59 eV is correlated to Se-O and/or Se-C interaction.[1-3]

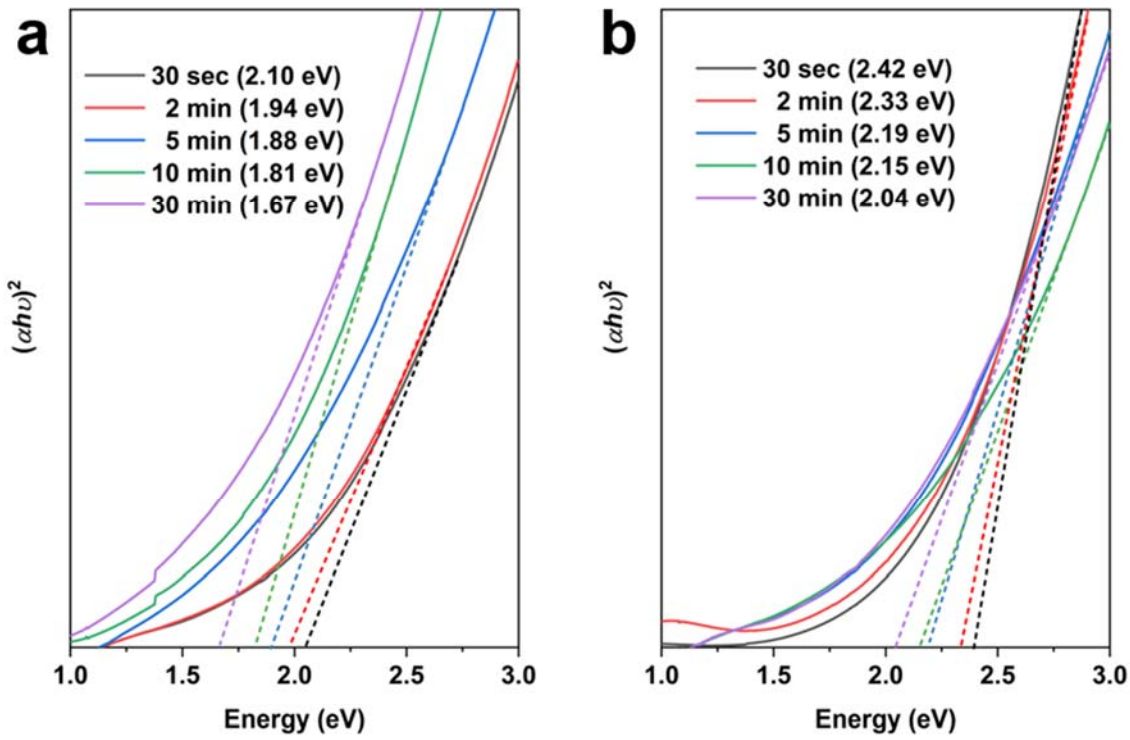

Figure S15. Plots of $(\alpha h\nu)^2$ vs photon energy (eV) for the (a) CZTS and (b) CZTS-CZTSe NCs obtained at different reaction times. The dotted lines represent the fits to the shorter wavelength linear regions of the absorbance spectra with the *x*-axis intercepts indicated in the legends.

References:

1. Huang, Y.; Wang, Z.; Jiang, Y.; Li, S.; Li, Z.; Zhang, H.; Wu, F.; Xie, M.; Li, L.; Chen, R., *Nano Energy* **2018,** *53*, 524-535.
2. Qiao, F.; Wang, J.; Ai, S.; Li, L., *Sens. Actuators B Chem.* **2015,** *216*, 418-427.
3. Liu, T.; Zhang, Y.; Hou, J.; Lu, S.; Jiang, J.; Xu, M., *RSC Adv,* **2015,** *5* (102), 84038-84043.