Electronic Supplementary Information

Selective epitaxial growth of zinc blende-derivative on wurtzite-derivative: The case of polytypic $Cu_2CdSn(S_{1-x}Se_x)_4$ nanocrystals

Liang Wu,[a]‡ Feng-Jia Fan,[a]‡ Ming Gong,[b] Jin Ge,[a] Shu-Hong Yu*[a]

[a] Division of Nanomaterials & Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China

[b] Engineering and Materials Science Experiment Center, University of Science and Technology of China, Hefei 230026, P. R. China

‡ These authors contributed equally to this work

* To whom correspondence should be addressed. E-mail: shyu@ustc.edu.cn

Experiment Section

Chemicals: Ethanol (99.7%), hexane (97%), 1-dodecanethiol (97%), CuCl (97%), CdI_2 (99.5%), $Cd(CH_3COO)_2\cdot 2H_2O$ ($Cd(Ac)_2$, 98.5%), CdO (99.5%), $SnCl_2\cdot 2H_2O$ (98%) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai). Oleylamine (80%-90%) was purchased from Aladdin Reagent Co. Ltd (Shanghai). Diphenyl disenenide (99%) was purchased from Acros Organics. All chemical reagents were used as received without further purification.

Synthesis of CCTSSe polytypic nanocrystals with tunable cadmium content: To prepare polytypic CCTSSe nanocrystals with variable cadmium contents, different amounts of CuCl, $SnCl_2\cdot 2H_2O$ and various amount of CdI_2 listed in Table S1 were dissolved in 10 mL oleylamine with the presence of 600 μL 1-dodecanethiol in a three-neck flask in air and then heated up to 180 °C. At the same while, 1.12 mmol diphenyl diselenide was dissolved in another three-neck flask containing 5 mL oleylamine in air at 70 °C. Reaction solutions were mixed by injecting diphenyl diselenide solution into the former salt solution. The temperature of the reaction solution was increased from 150 °C to 280 °C at a heating rate of 10 °C/min and kept at 280 °C for 30 min. In order to explore the effect of the concentration of 1-DDT on the synthesis of polytypic CCTSSe nanocrystals, different concentration of 1-DDT was used (Table S1). Time dependent experiments with the same recipe to sample 2 were performed to study the growth process of these polytypic nanocrystals. According to the solution color change during the reaction, the growth of nanocrystals should start at about 220 °C, so we quenched the reaction when the reaction temperatures were just rose to 230, 250 and 280 °C. We also select $Cd(Ac)_2$ and CdO instead of CdI_2 to synthesis of polytypic CCTSSe nanocrystals with the same mole ratio of resources with the sample 2. When the reaction was completed, the flask was removed from the heating mantle and naturally cooled down. The black product was collected and centrifuged at 8000 rpm for 5 min and the upper clear solution was discarded. Then hexane was added to disperse the nanocrystals. To collect the nanocrystals again, ethanol was added into the dispersion and the formed slurry were centrifuged again at 8000 rpm for 5 min. The nanocrystals were washed through repeating the above dispersing and depositing process for two times

Measurement and characterization: The product was characterized by powder X-ray power diffraction (XRD), using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite mono-chromatized Cu Kα radiation (λ = 1.54056 Å). The operation voltage and current were kept at

40 kV and 400 mA, respectively. The simulate WZ and ZB CCTSe powder XRD pattern were obtained from Diamond 3.2. Nanocrystals dispersed in hexane were dropped on Cu or Mo grid for transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) observation, which were performed on JEOL-2010F with an acceleration voltage of 200 KV. Energy dispersive spectrometer (EDS) was carried out on Inca Oxford equipped on JEOL-2010F. Optical absorption spectra of nanocrystals dispersed in hexane were measured at room temperature using a DUV—3700 ultraviolet-visible-near infrared (UV-vis-NIR) spectrometer (Shimadzu).

Table S1. Amounts of CuCl, CdI_2, $SnCl_2 \cdot 2H_2O$, 1-dodecanethiol and diphenyl diselenide used for synthesizing the polytypic CCTSSe nanocrystals.

Sample	CuCl *(mmol)*	CdI_2 *(mmol)*	$SnCl_2 \cdot 2H_2O$ *(mmol)*	1-dodecanethiol *(ml)*	Diphenyl disenenide *(mmol)*
1#	0.28	0.112	0.14	0.6	1.12
2#	0.28	0.14	0.14	0.6	1.12
3#	0.28	0.168	0.14	0.6	1.12
4#	0.28	0.196	0.14	0.6	1.12
5#	0.28	0.224	0.14	0.6	1.12
6#	0.28	0.14	0.14	1.0	1.12
7#	0.28	0.14	0.14	0.3	1.12

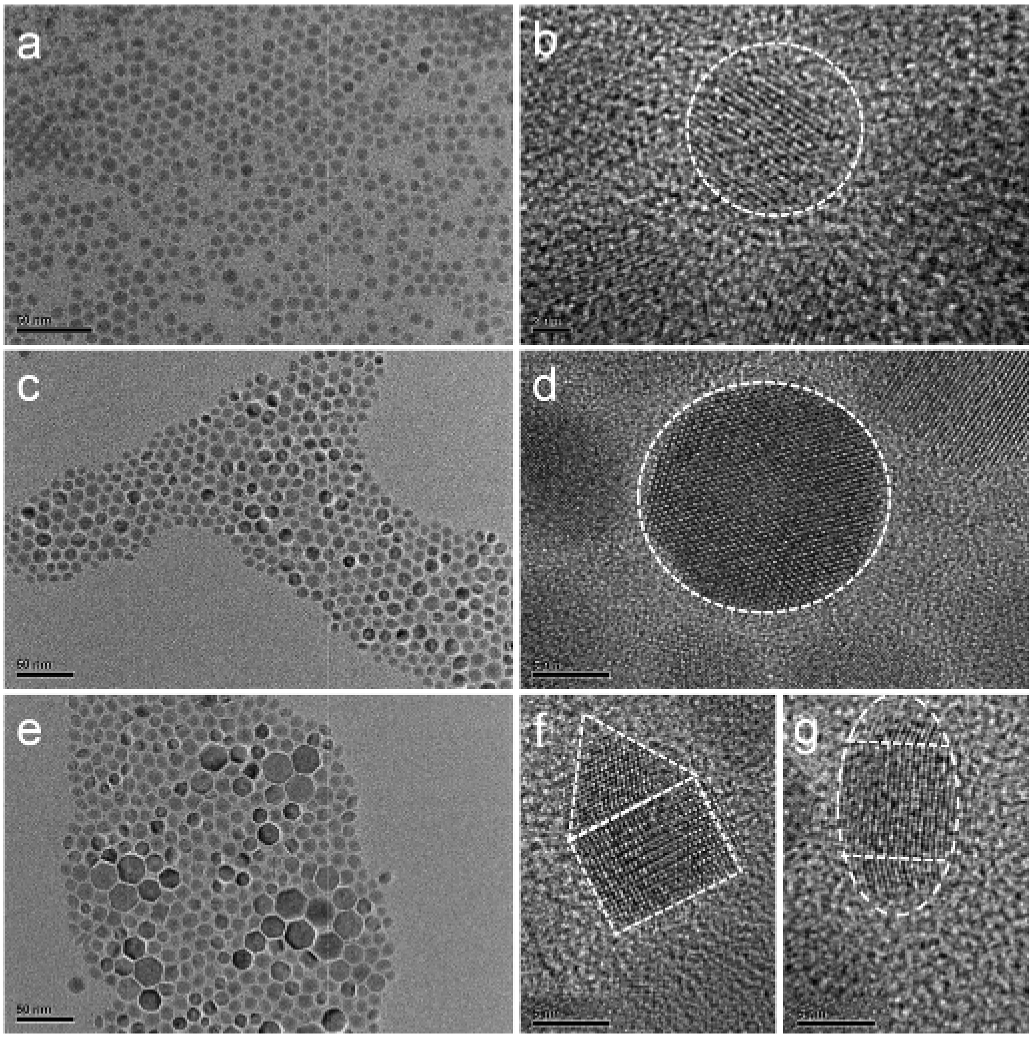

Fig. S1 TEM and HRTEM images of nanocrystals prepared at different elevated reaction temperature. (a) and (b) 230 °C, (c) and (d) 250 °C, (e)-(g) 280 °C.

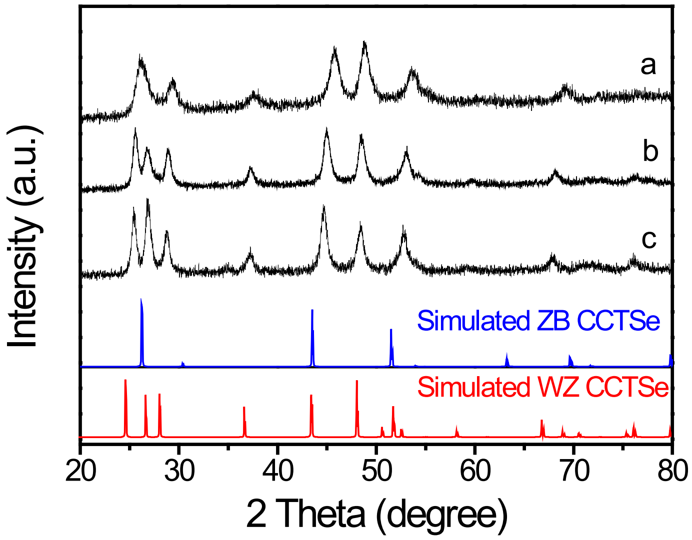

Fig. S2 PXRD patterns of nanocrystals prepared at different elevated reaction temperature. (a) and (b) 230 °C, (c) and (d) 250 °C, (e)-(g) 280 °C.

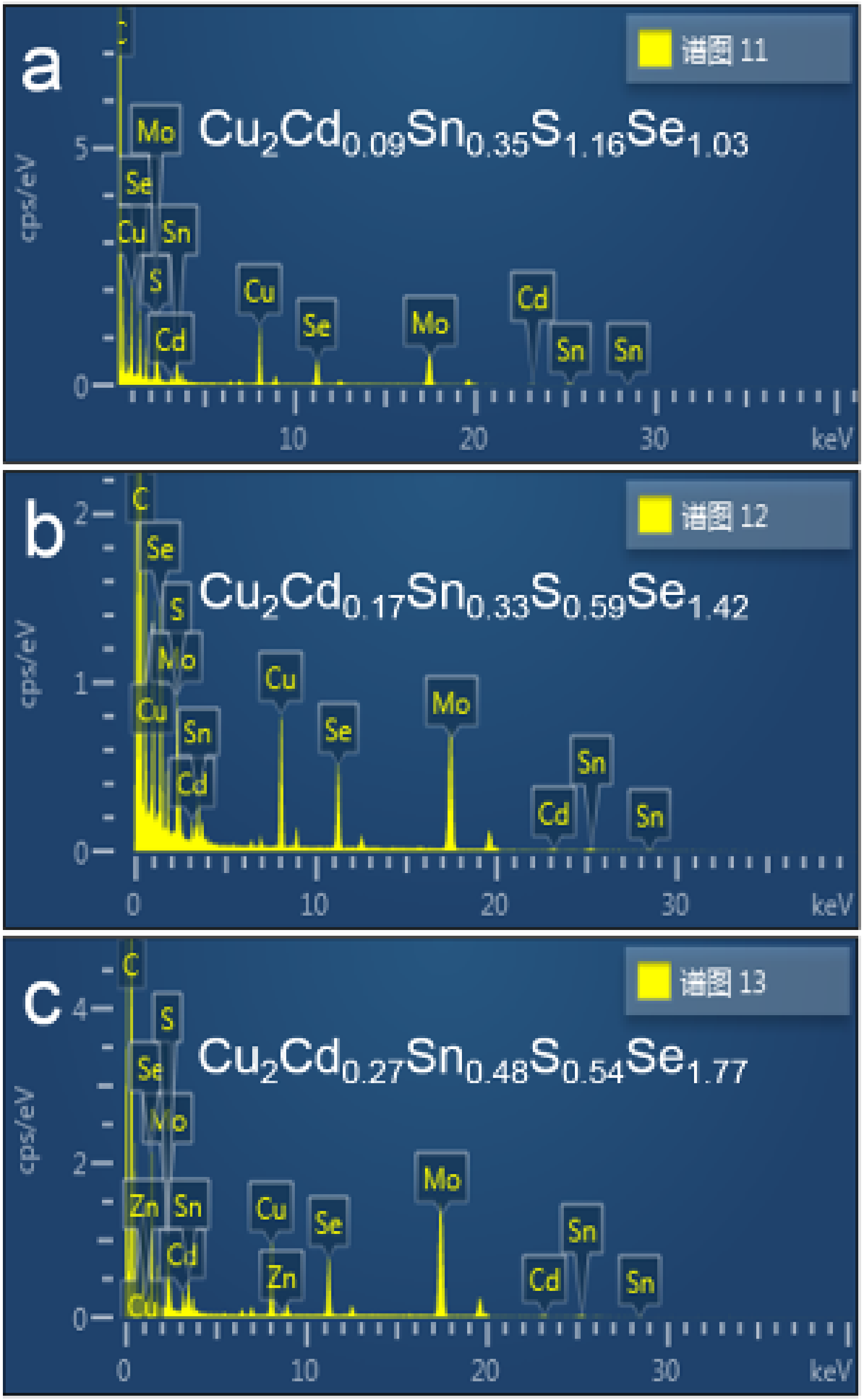

Fig. S3 EDS spectra of nanocrystals prepared at different elevated reaction temperature. (a) 230 °C, (b) 250 °C, (c) 280 °C.

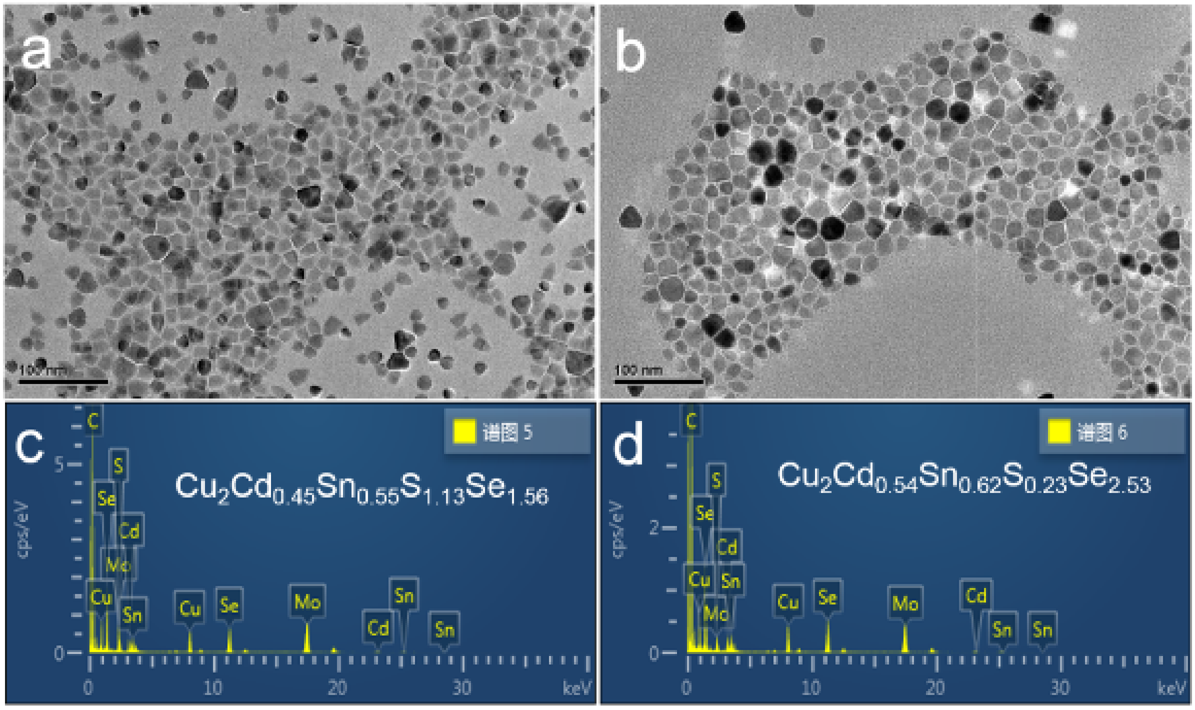

Fig. S4 (a) and (b) TEM images of the polytypic nanocrystals synthesized with 1 ml 1-DDT and 0.3 ml 1-DDT, respectively. (c) and (d) EDS spectra of the polytypic nanocrystals synthesized with 1 ml 1-DDT and 0.3 ml 1-DDT, respectively.

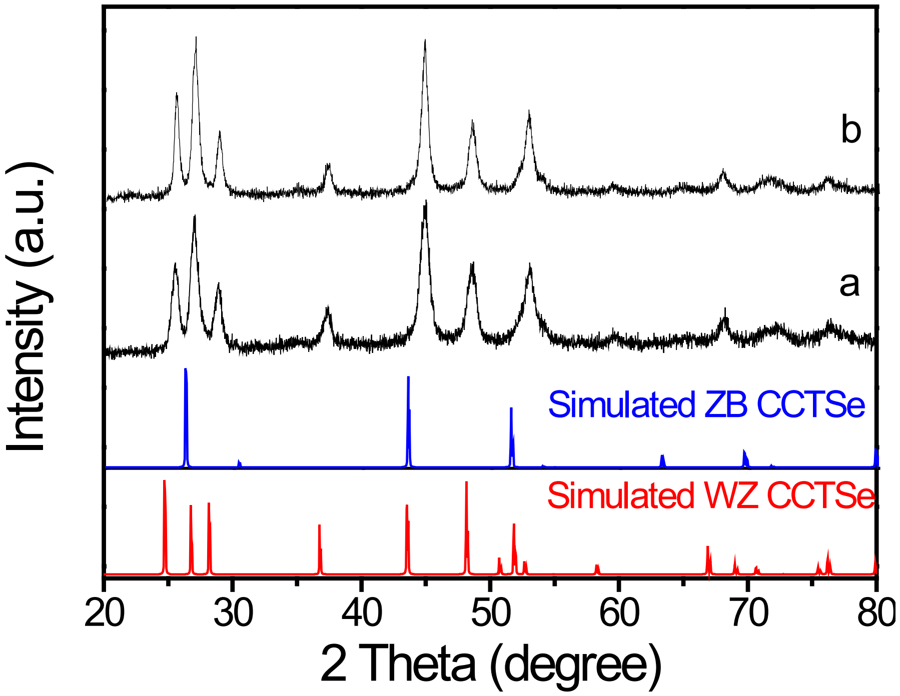

Fig. S5 (a) and (b) PXRD patterns of the polytypic nanocrystals synthesized with 1 ml 1-DDT and 0.3 ml 1-DDT, respectively.

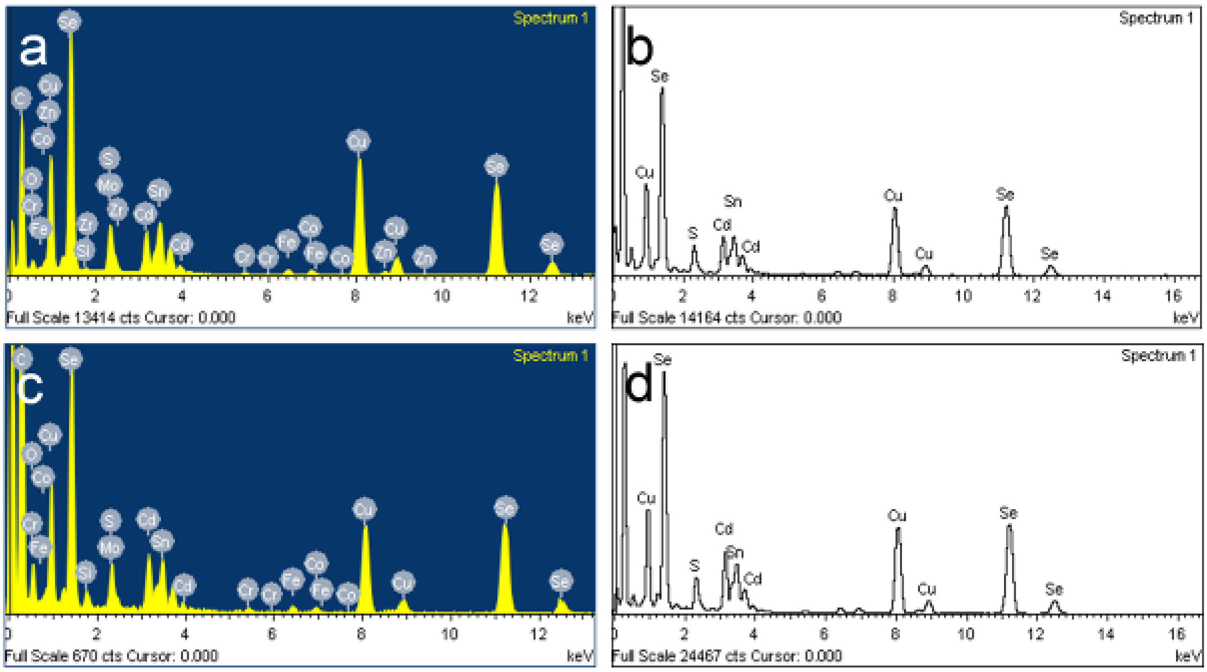

Fig. S6 EDS spectra of the polytypic CCTSSe nanocrystals: (a) $Cu_2Cd_{0.6}Sn_{0.7}S_{0.3}Se_{2.5}$, (b) $Cu_2Cd_{0.8}Sn_{0.8}S_{0.8}Se_{2.7}$, (c) $Cu_2CdSn_{0.9}S_{0.4}Se_{3.1}$, (d) $Cu_2Cd_{1.1}Sn_{0.9}S_{0.6}Se_{3.1}$.

Table S2. The chemical compositions and band-gaps of the polytypic CCTSSe nanocrystals.

Sample	Chemical composition of product	Estimated band-gap(eV)
1#	$Cu_2Cd_{0.59}Sn_{0.74}S_{0.26}Se_{2.45}$	1.08
2#	$Cu_2Cd_{0.79}Sn_{0.80}S_{0.75}Se_{2.70}$	0.97
3#	$Cu_2CdSn_{0.94}S_{0.41}Se_{3.07}$	1.08
4#	$Cu_2Cd_{1.13}Sn_{0.85}S_{0.60}Se_{3.11}$	1.05

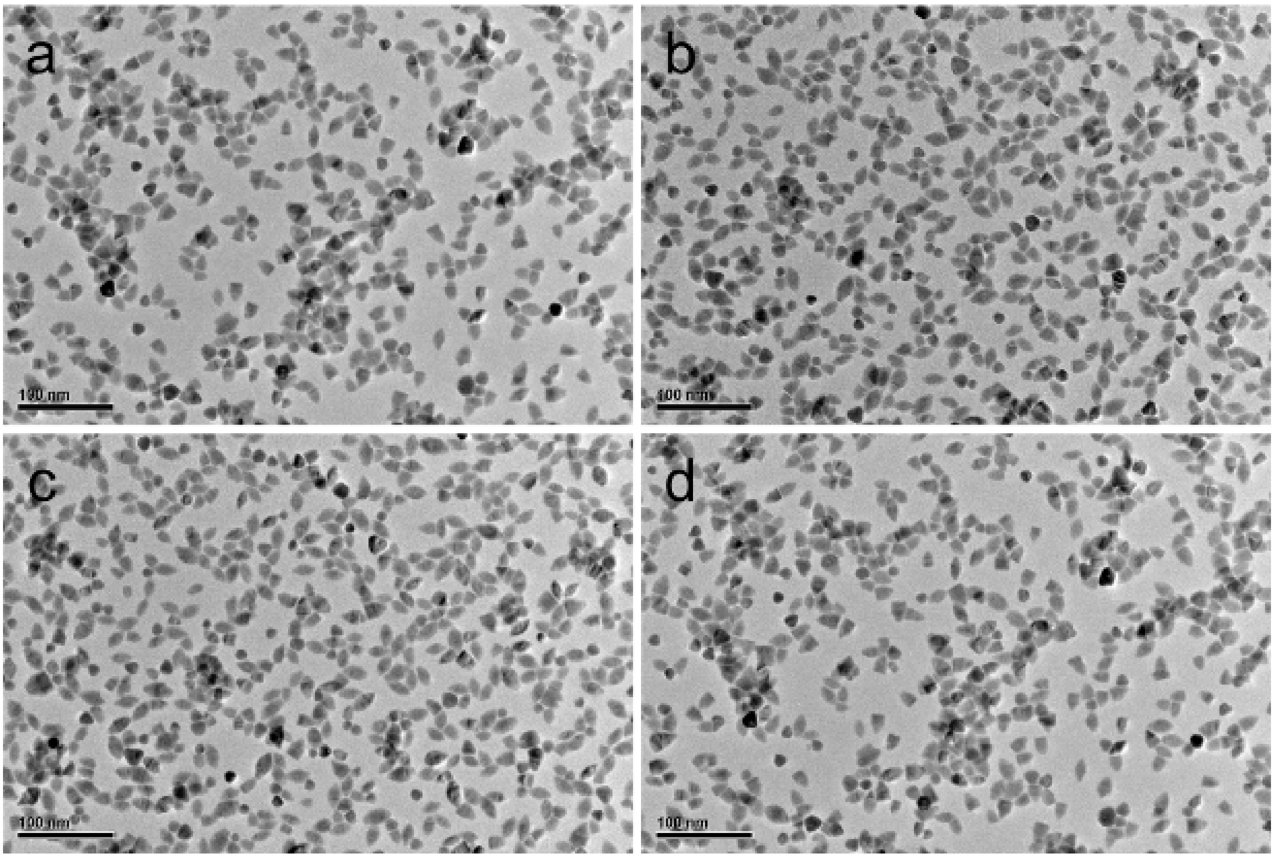

Fig. S7 Low magnification TEM images of the polytypic CCTSSe nanocrystals for statistic calculation of the proportions of rugby-like and bullet-like nanocrystals: (a) $Cu_2Cd_{0.59}Sn_{0.74}S_{0.26}Se_{2.45}$, (b) $Cu_2Cd_{0.79}Sn_{0.80}S_{0.75}Se_{2.70}$, (c) $Cu_2CdSn_{0.94}S_{0.41}Se_{3.07}$, (d) $Cu_2Cd_{1.13}Sn_{0.85}S_{0.60}Se_{3.11}$.

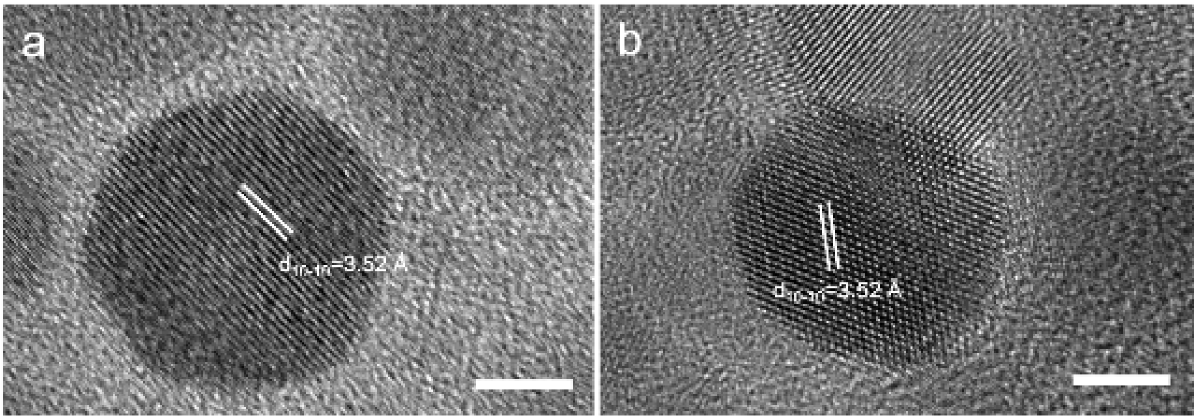

Fig. S8 (a) and (b) HRTEM images of two different nanoparticles.

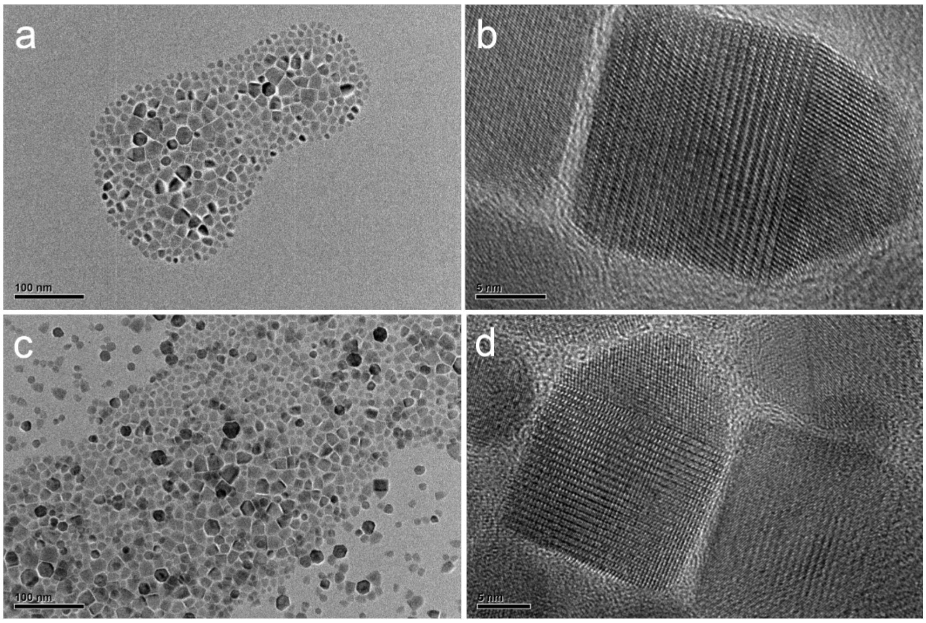

Fig. S9 TEM and HRTEM images of the polytypic CCTSSe nanocrystals synthesized with different Cd source. (a) and (b) Cd(Ac)$_2$, (c) and (d) CdO.

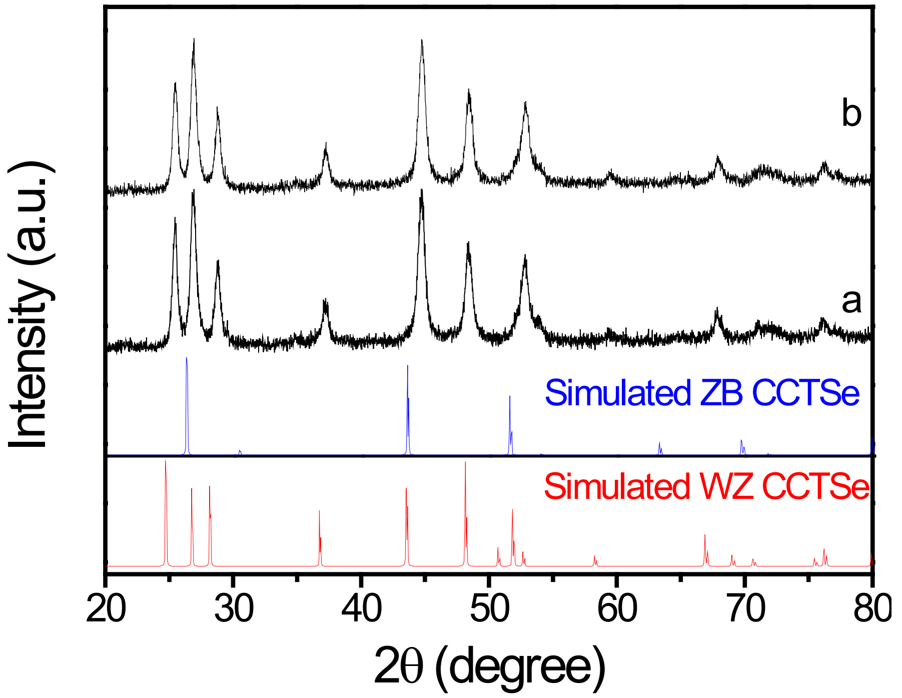

Fig. S10 PXRD patterns of polytypic CCTSSe nanocrystals synthesized with different Cd source. (a) and (b) Cd(Ac)$_2$, (c) and (d) CdO.

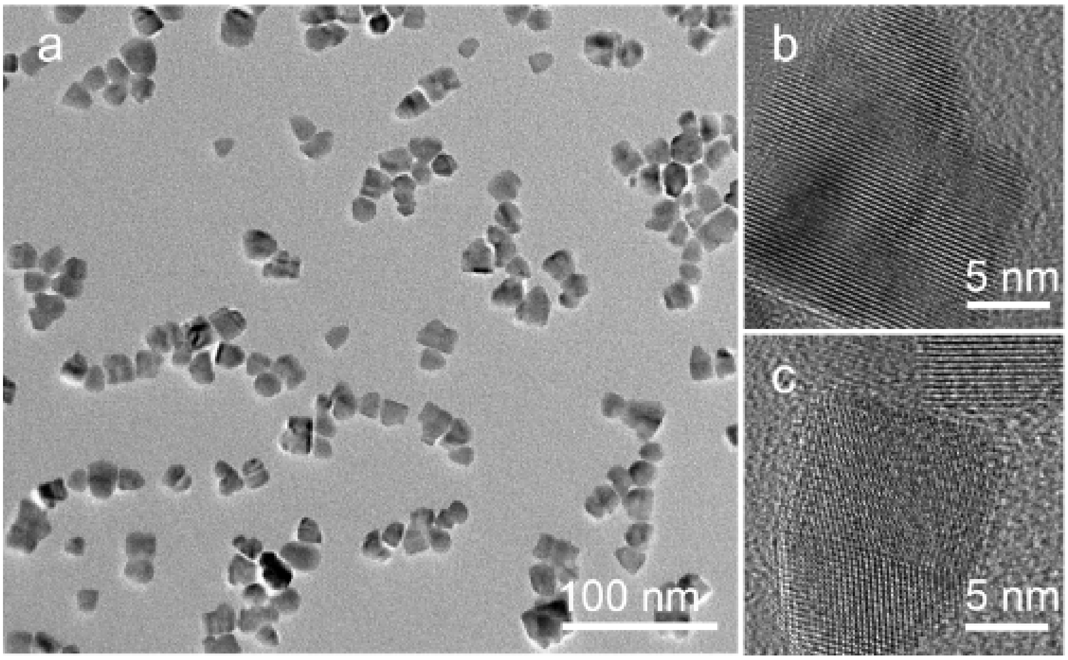

Fig. S11 TEM and HRTEM images of the polytypic CCTSSe nanocrystals synthesized with the Cu:Cd:Sn ratio in precursors kept as 2:1.6:1.

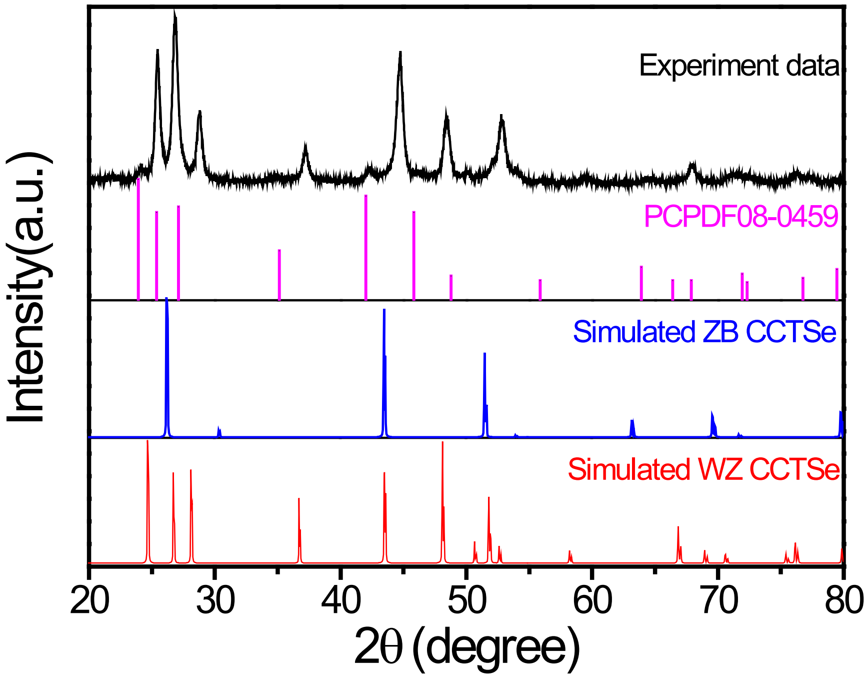

Fig. S12 PXRD pattern of the polytypic CCTSSe nanocrystals synthesized with the Cu:Cd:Sn ratio in precursors kept as 2:1.6:1. For reference, the diffraction pattern of CdSe and the simulated diffraction patterns of WZ and ZB CCTSe are showed also.

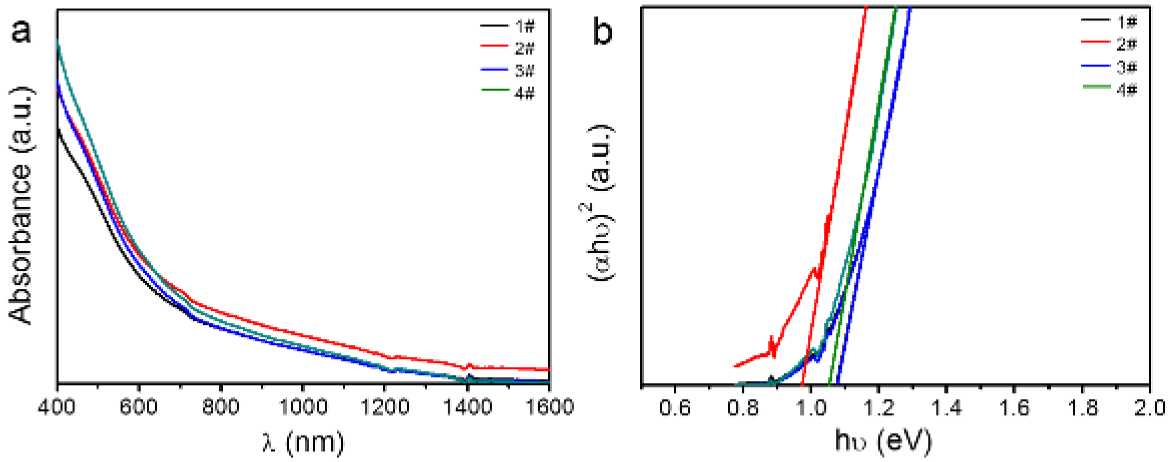

Fig. S13 (a) UV-vis-NIR absorbance spectra of polytypic CCTSSe nanocrystals, (b) $(\alpha h\nu)^2$ versus photon energy to low energy of polytypic CCTSSe nanocrystals.