Electronic Supplementary Information (ESI)

CdSe/CdSe$_x$Te$_{1-x}$ Nanorod Heterostructures: Tuning Alloy Composition and Spatially Indirect Recombination Energies

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Experimental Details

General considerations. The single pot reactions were carried out in a standard Schlenk line under N_2 atmostsphere. Technical grade trioctylphosphine oxide (TOPO) (90%), technical grade trioctylphosphine (TOP) (90%), CdO (99.5%), Se powder (99.99%), and Te powder (99.9%) were obtained from Sigma Aldrich. ACS grade chloroform, methanol, butanol, and toluene were obtained from Fischer Scientific. N-octadecyl phosphonic acid (ODPA) was obtained from PCI Synthesis. Materials were used as received.

Seed CdSe nanorods. First, 2.0 g (5.2 mmol) of TOPO, 0.67 g (2.0 mmol) of ODPA and 0.13 g (1.0 mmol) of CdO were added to a 50 ml three-neck round-bottom flask. The reaction mixture was degassed at 150 °C for 1 h under vacuum with occasional N_2 purges then heated to 350 °C under N_2 with vigorous stirring. The solution became transparent and colorless after 2 h indicating ODPA-Cd complex formation. The reaction mixture was cooled to 150 °C and degassed for an additional 10 min to remove O_2 and H_2O produced during complexation then heated again under N_2. At 320 °C, a solution containing 1.5 ml of 0.33 M (TOPSe) and 0.25 ml of anhydrous toluene was swiftly injected. The reaction mixture was quenched to 260 °C where the growth was carried out. After 20 min at 260 °C, an aliquot of the seed CdSe NRs was taken for analysis. The aliquot was cleaned by dissolving in chloroform then precipitating with methanol (80%) and butanol (20%) and centrifuging at 2000 rpm. The supernatant was discarded and the precipitate was dissolved in chloroform. Unreacted ODPA-Cd has similar solubility as the NRHs and may persist through cleaning. By ultra-centrifuge at 10,000 rpm, ODPA-Cd rises and solidifies above dissolved NRHs in chloroform. Additional cleaning cycles are conducted to prepare samples for HR TEM and HAADF STEM.

Synthesis of linear CdSe/CdSe$_x$Te$_{1-x}$ NRHs. To the reaction mixture containing CdSe NR seeds at 250 °C under N_2, 0.8 ml of 1 M TOP-Se and 0.0 to 0.4 ml of 1 M TOP-Te diluted with additional TOP to make the total volume 2 ml was injected at a rate of 8 ml/h via syringe pump. The reaction mixture was aged for an additional 5 min at 250 °C before the heating mantle was removed and the flask was rapidly cooled by air jet. Upon completion of reaction, the final product was cleaned by precipitation with methanol (80%) and butanol (20%), then stored as a solution in chloroform under N_2 atmosphere. Additional cleaning cycles are conducted to prepare samples for HR TEM and HAADF STEM.

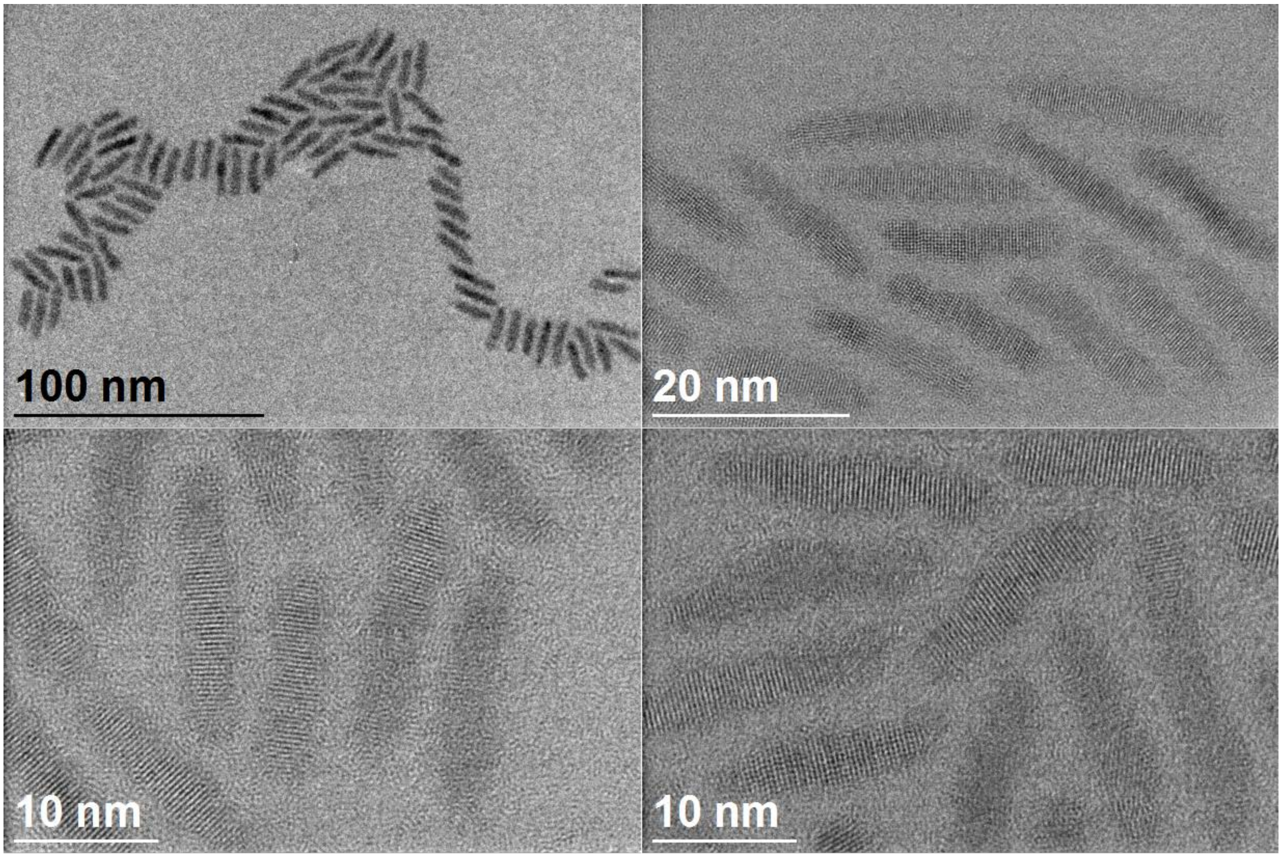

Figure S1. TEM images of typical CdSe NR seeds at various magnifications. Only images at 600kX magnification (eg. bottom two images) were used for lattice fringe/constant calibration and characterization.

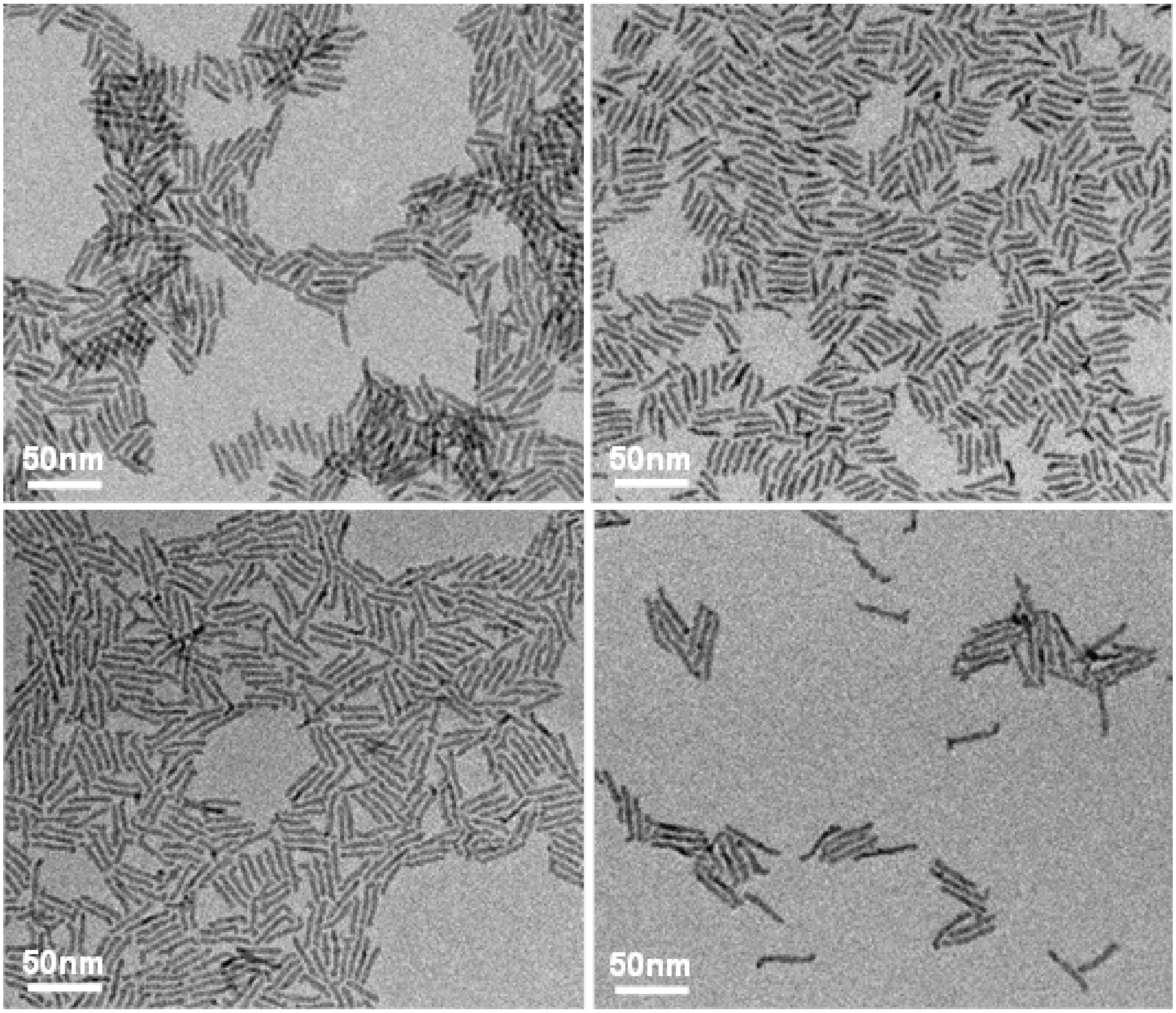

Figure S2. Low mag TEM images of NRHs synthesized with 0.1(a), 0.2 (b), 0.3 (c) and 0.4 (d) mmol of Te during the formation of the second component.

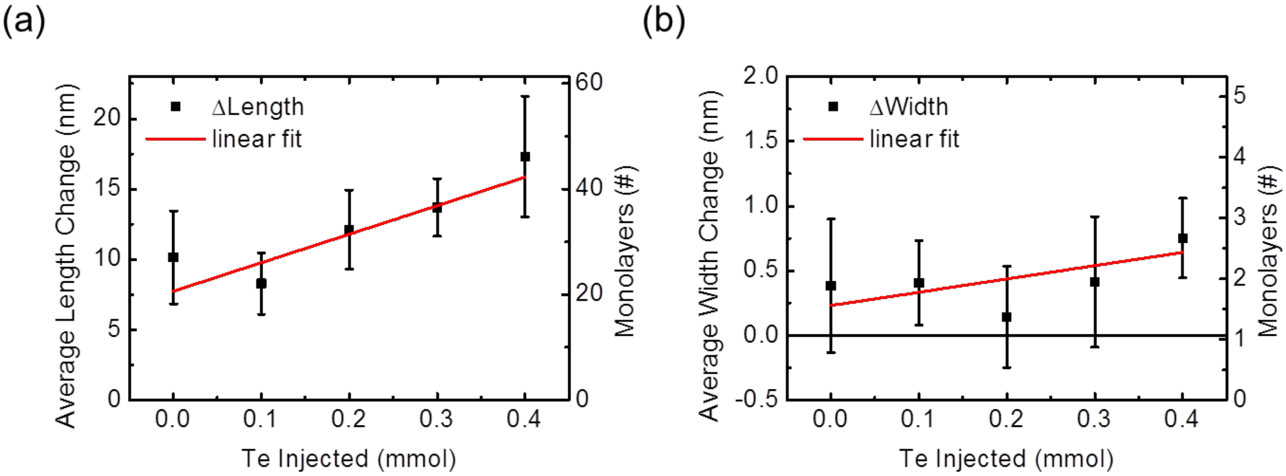

Figure S3: The average length (a) and width (b) of alloyed NRHs measured from TEM images as a function of amount of Te co-injected with a fixed amount of Se (0.80 mmol). The length and width increases in number of monolayers are shown on the right y-axis of each figure. Linear fits are shown in red. At least 25 CdSe NR seeds and 25 NRHs were measured to generate these size statistics.

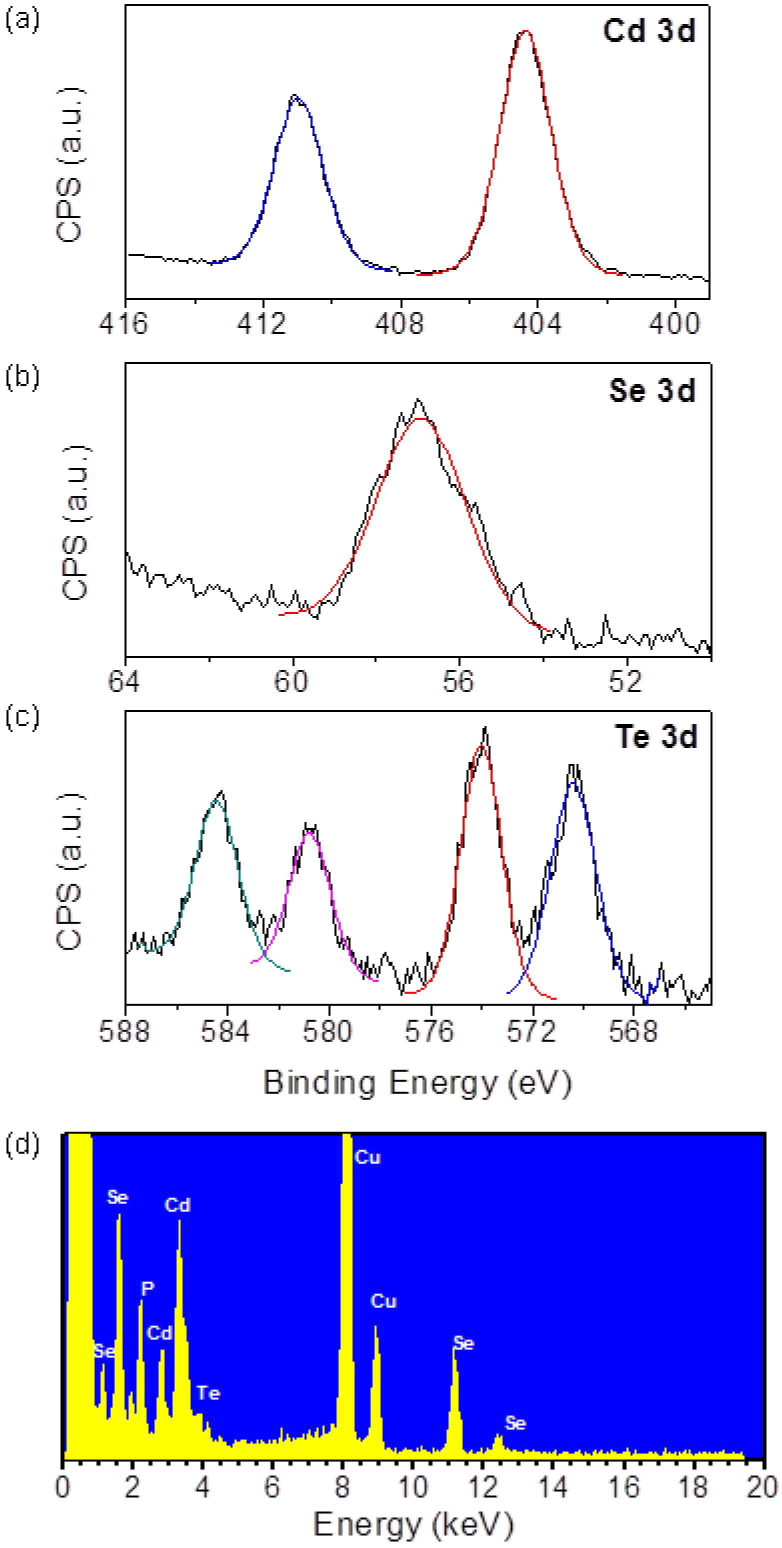

Figure S4. Representative XPS (a – c) and EDS (d) spectra of NRHs synthesized using 0.2 mmol of Te.

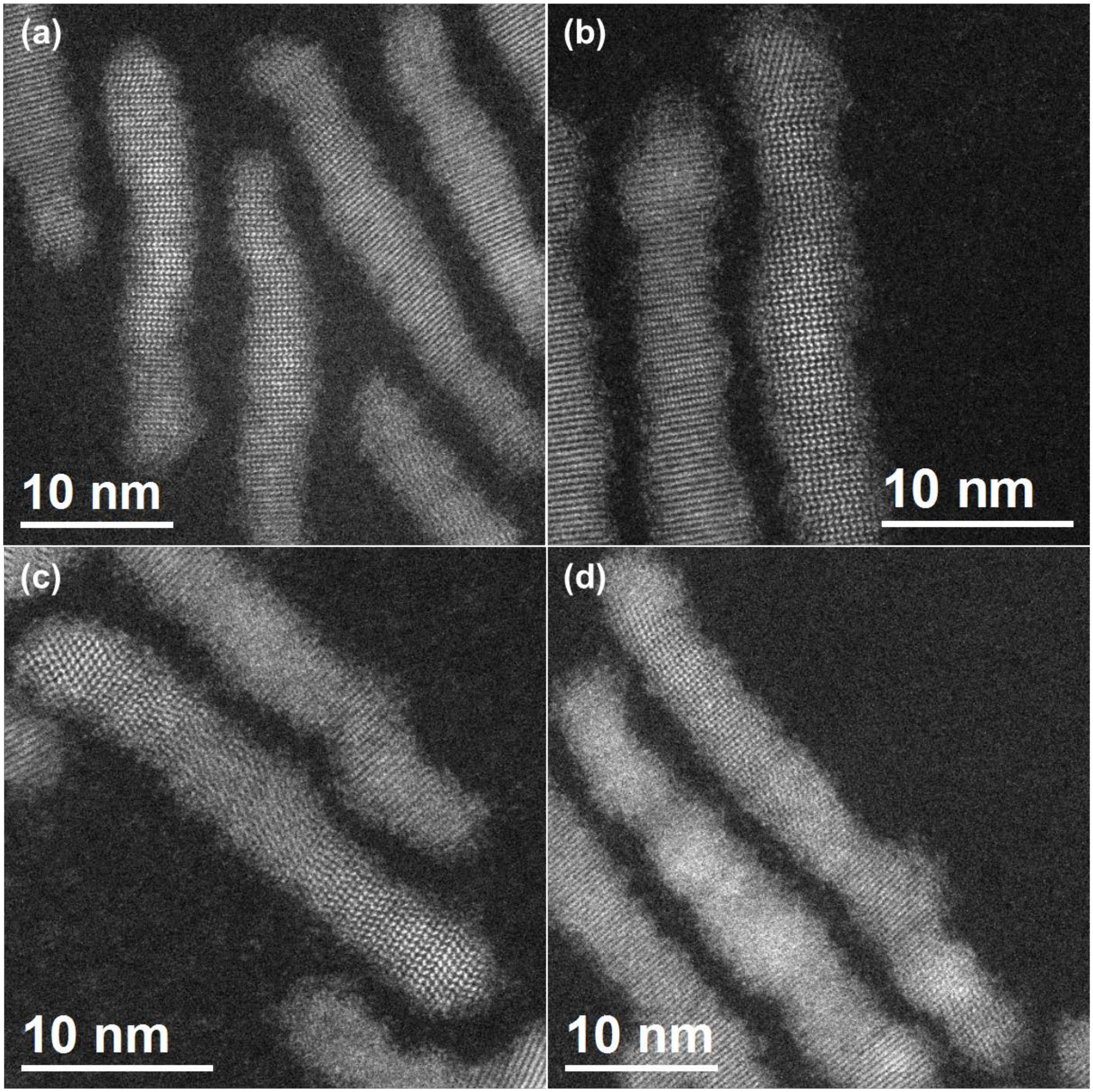

Figure S5. Lower magnification STEM images of NRHs synthesized with 0.1(a), 0.2 (b), 0.3 (c) and 0.4 (d) mmol of Te during the formation of the second component.

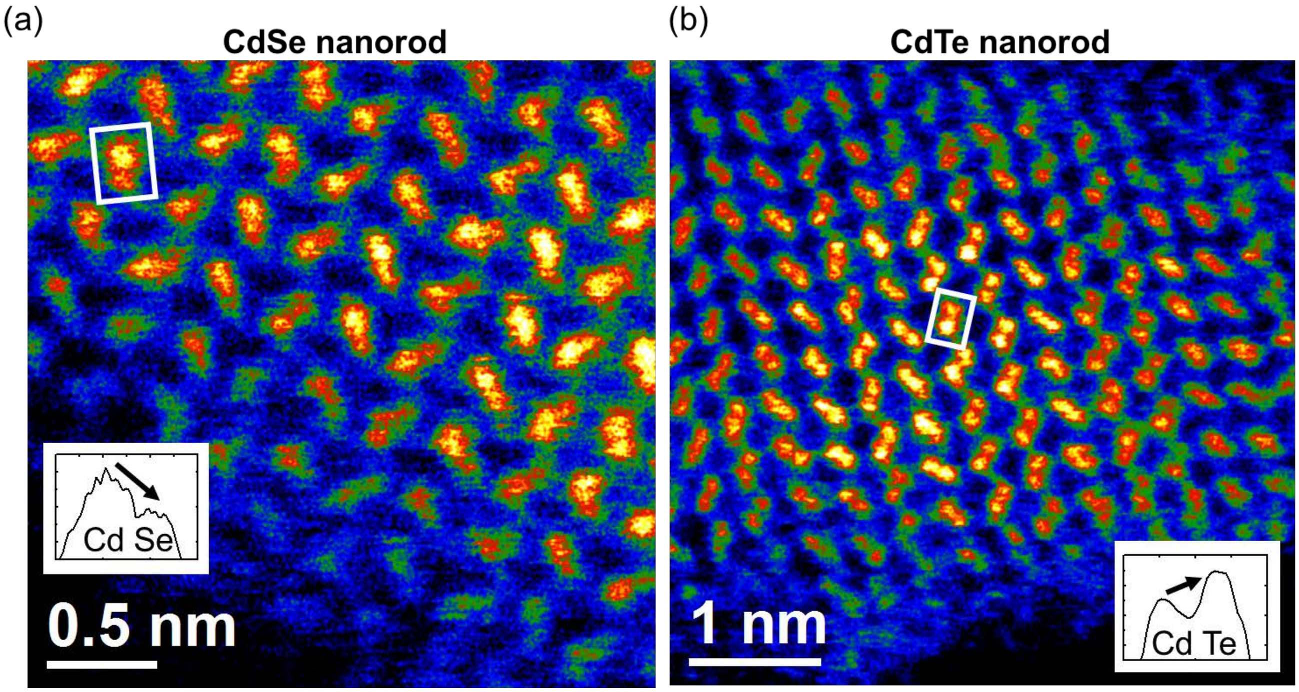

Figure S6: Characteristic high-resolution aberration-corrected HAADF STEM images of a CdSe NR (a) and CdTe NR (b) used to establish the baseline Z-contrast (control sample). Integrated line scans for each boxed region are shown in the inset as examples.

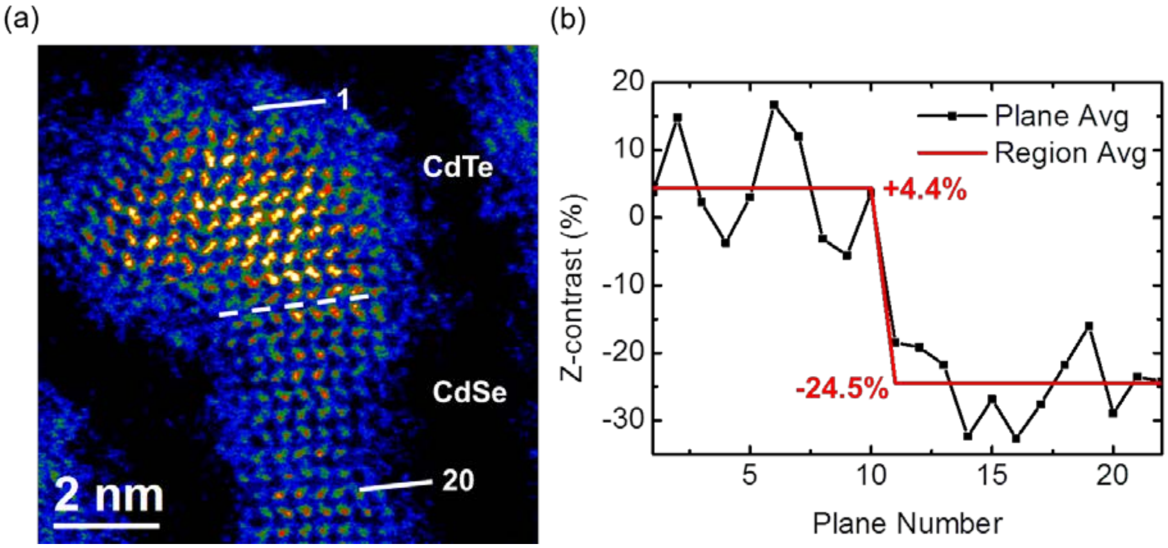

Figure S7: (a) High magnification STEM image of a non-alloyed NRH made from 0.5 mmol of Te (no Se) injected for the second component. The estimated junction location is shown by the dashed line. The solid line and the numbers indicate the lattice plane numbering used in (b). (b) Average Z-contrast (corrected for background) as a percent change in the scattering intensity (electron count) from the Cd (cation) column to the chalcogen (anion) column for each lattice plane in a (black). The contrast is averaged on each side of the estimated junction region and shown as horizontal (red) lines with the average values indicated.

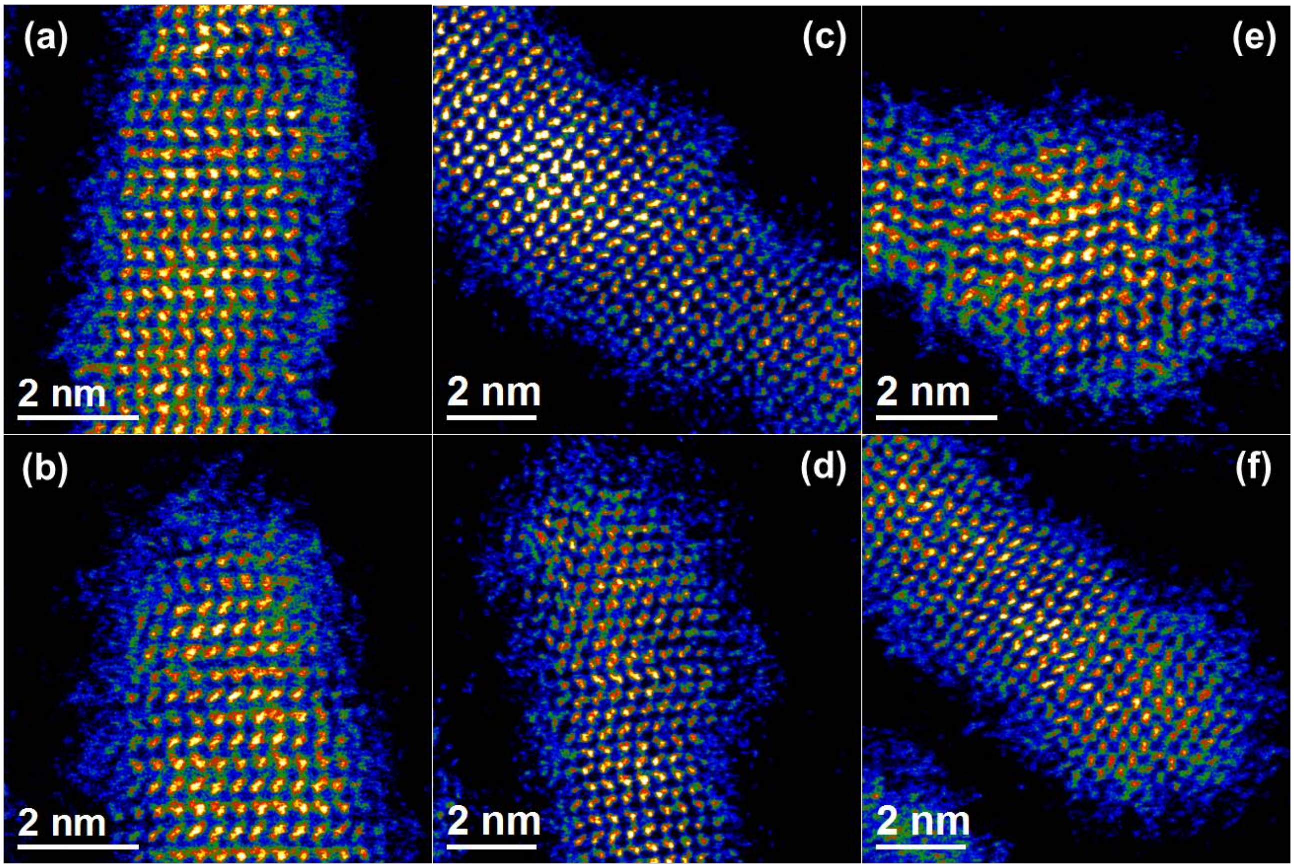

Figure S8. Characteristic high magnification STEM images of alloyed tips used to measure Z-contrast for NRHs synthesized with 0.1 (a,b), 0.2 (c,d), and 0.3 (e,f) mmol of Te during the formation of the second component. An example of the 0.4 mmol Te case can be seen in Figure 5.