Colloidal CdSe/Cu_3P/CdSe Nanocrystal Heterostructures and their Evolution upon Thermal Annealing

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SUPPORTING INFORMATION

Synthesis of Cu_3P nanoplatelets

In a typical synthesis a solution of CuCl (1.6 mmol), oleylamine (9.7 mmol), and octylamine (9.7 mmol) was prepared under inert atmosphere and then heated at 180°C for 2 h to get a clear yellowish solution. A mixture of 8g of TOPO and 8 mL of TOP was degassed in a reaction flask for 2 h at 150°C under vacuum using a standard Schlenk line. The copper solution was then cooled to 150°C and then rapidly injected into the reaction flask at 370°C. The reaction was heated at 350°C for 1 hour and then rapidly cooled to room temperature. The nanocrystals were precipitated with addition of ethanol and then washed three times by dispersion in toluene followed by precipitation by addition of ethanol. The NCs were eventually dispersed in 4 ml of 1-octadecene (obtaining a ODE-Cu_3P dispersion with a concentration of Cu^+ ions of 12mM) and kept in a glove box.

Synthesis of CdSe/Cu_3P heterostructures

Sample	ODPA (mg)	HPA (mg)	Temperature (°C)	Time (min)
Figure 1b	145	40	300	8
Figure 1c	145	40	340	8
Figure 2a	181	50	380	1
Figure 2b and 3	181	50	380	8
Figure S1a	181	0	380	8
Figure S1b	181	50	350	8

Table S1. The synthetic parameters used to obtain the samples shown in the main text and in the supporting information are reported in the table. In all the syntheses we used 30mg of CdO, 0.3ml of TOP-Se solution (containing 12mg/ml of Se) and the amount of ODE-Cu_3P dispersion was 0.5 ml.

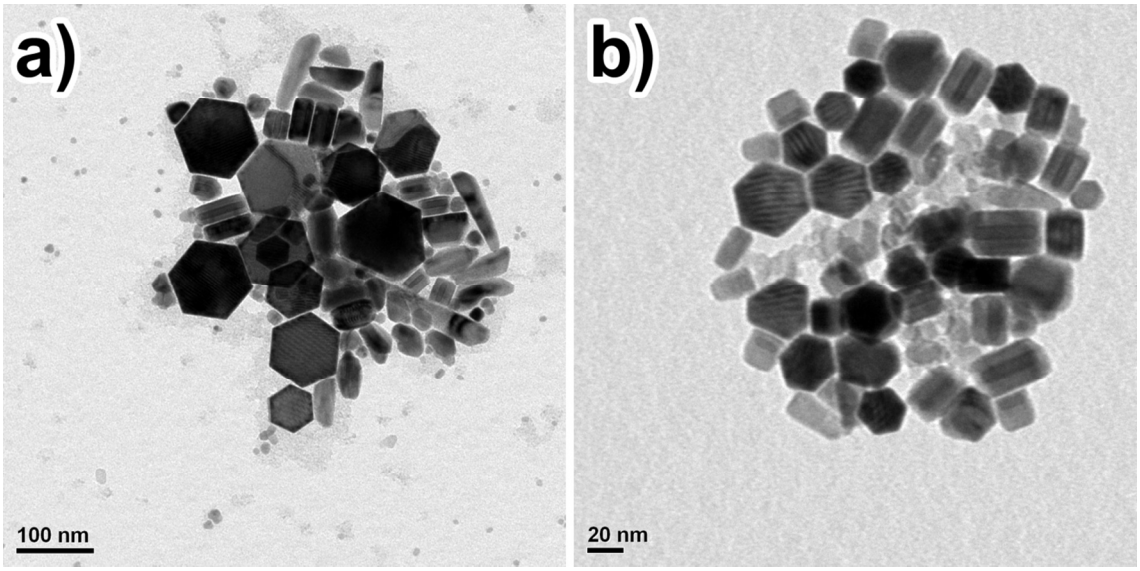

Figure S1. *Low resolution TEM images of sandwich-like CdSe/Cu_3P/CdSe nanocrystals (NCs) obtained varying the synthetic conditions.* ***a)*** *The NCs were synthesized using only ODPA at 380°C.* ***b)*** *Sandwich-like NCs were grown at lower temperature 350°C using both ODPA and HPA.*

TEM analysis of Moiré pattern

The corresponding Moiré fringes spacing (D_m) was calculated along the parallel directions [11-20]//[10-10] of two phases according to the following relation:

$$D_m=(d_1 \times d_2) / |d_1 - d_2|$$

where d_1 and d_2 are the interfering lattice planes generating the Moiré fringes. D_m experimental measurements fitted with the calculated value of 3.09 nm (Figure S2). The structural similarities of {0002} CdSe and Cu_3P slices are displayed in Figure S2c, where their corresponding 2D lattices, with compatible hexagonal framework, are reported. Then, {0002} facets represent actual interfaces for the preferential growth of CdSe/Cu_3P/CdSe epitaxial-related heterostructures with low strained interfaces.

The Moiré component was still evident in the high magnification HRTEM images of the sandwiches, where properly oriented along the [0001] zone axes (Figure S2d). In the reciprocal space the FFT patterns exhibited the superposition and the interference of both CdSe and Cu_3P [0001] zone axis projections. By FFT filtering it was possible to isolate the contribution of single phases and Moiré fringes too, as displayed in the insets of Figure S2d. Here the spots of CdSe are circled in blue and those of Cu_3P in red, respectively. The yellow circles define a double diffracted contribution generated by the diffraction of CdSe-Bragg-scattered beams by the Cu_3P platelet. Close to the central spot, the green circles highlight the reflections of Moiré fringes with periodicity of 3.01 nm. The main lattice planes of CdSe and Cu_3P, besides the Moiré fringes, have been again extracted from direct HRTEM image obtained by FFT-filtering process.

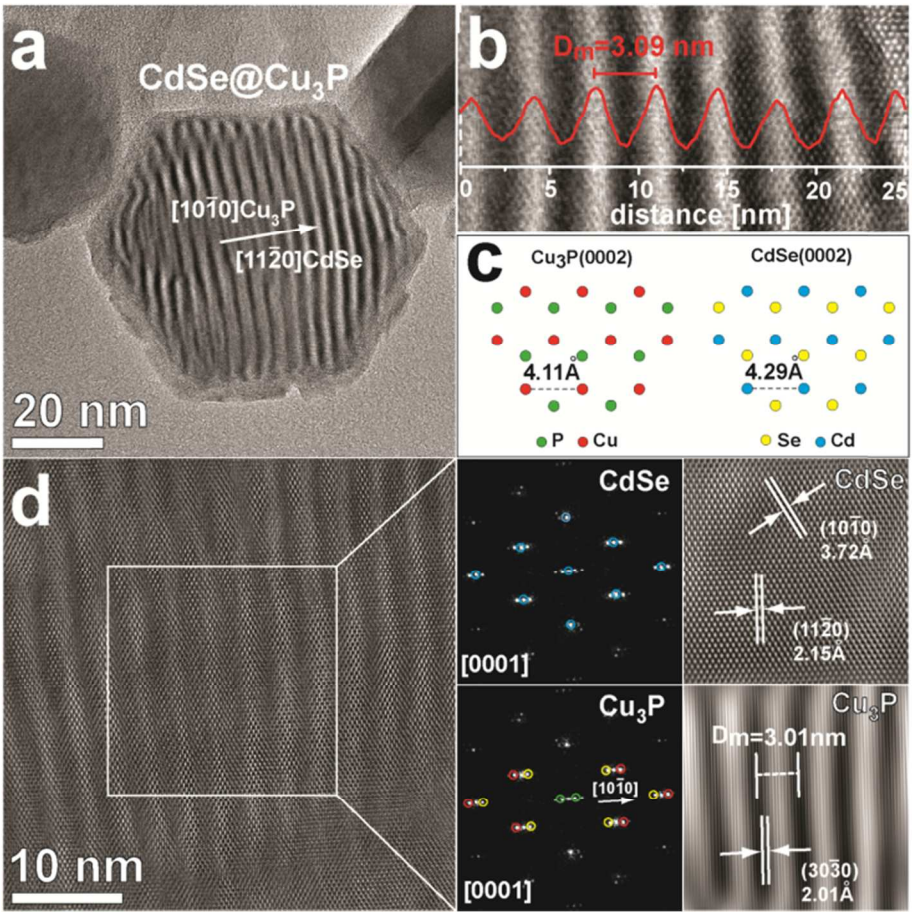

Figure S2. *Plan-view HRTEM images of CdSe/Cu_3P/CdSe sandwiches.* ***a)*** *Moiré fringes along the parallel [10-10]//[11-20] directions;* ***b)*** *Moiré fringe periodicity, D_m=3.09 nm;* ***c)*** *2D lattices of {0002} Cu_3P and CdSe slices showing their strong similarities;* ***d)*** *HRTEM detail of [0001] oriented heterostructure showing Moiré fringes; in the insets are displayed the contribution of CdSe (blue circles), Cu_3P (red circles), double diffractions (yellow circles) and those of the Moiré fringes (green circles). FFT filtered HRTEM images were built by considering only the blue spots of CdSe, and both red and green spots, along the [10-10] direction, for the Cu_3P where the (30-30) lattice planes and the D_m Moiré fringes are displayed.*

STEM-EDX analysis after annealing

Elemental analysis of dissociated NCs was performed via STEM-EDX considering areas containing decades of NCs and single NCs. STEM-EDX spectra were acquired after the thermal treatment, when the system reached again RT condition, in order to avoid the "blinding" effect of Si(Li) detector produced by thermal infrared radiation emitted by heater holder, TEM-grid and sample during the annealing experiment. Two STEM-EDX representative cases of many NCs (Figure S3a) and single NP (Figure S3b) are reported. As shown clearly in the EDX spectra no evidence of any Cd peaks are observed. This was consistent with a selective loss of Cd from NCs by thermal sublimation in high vacuum condition.

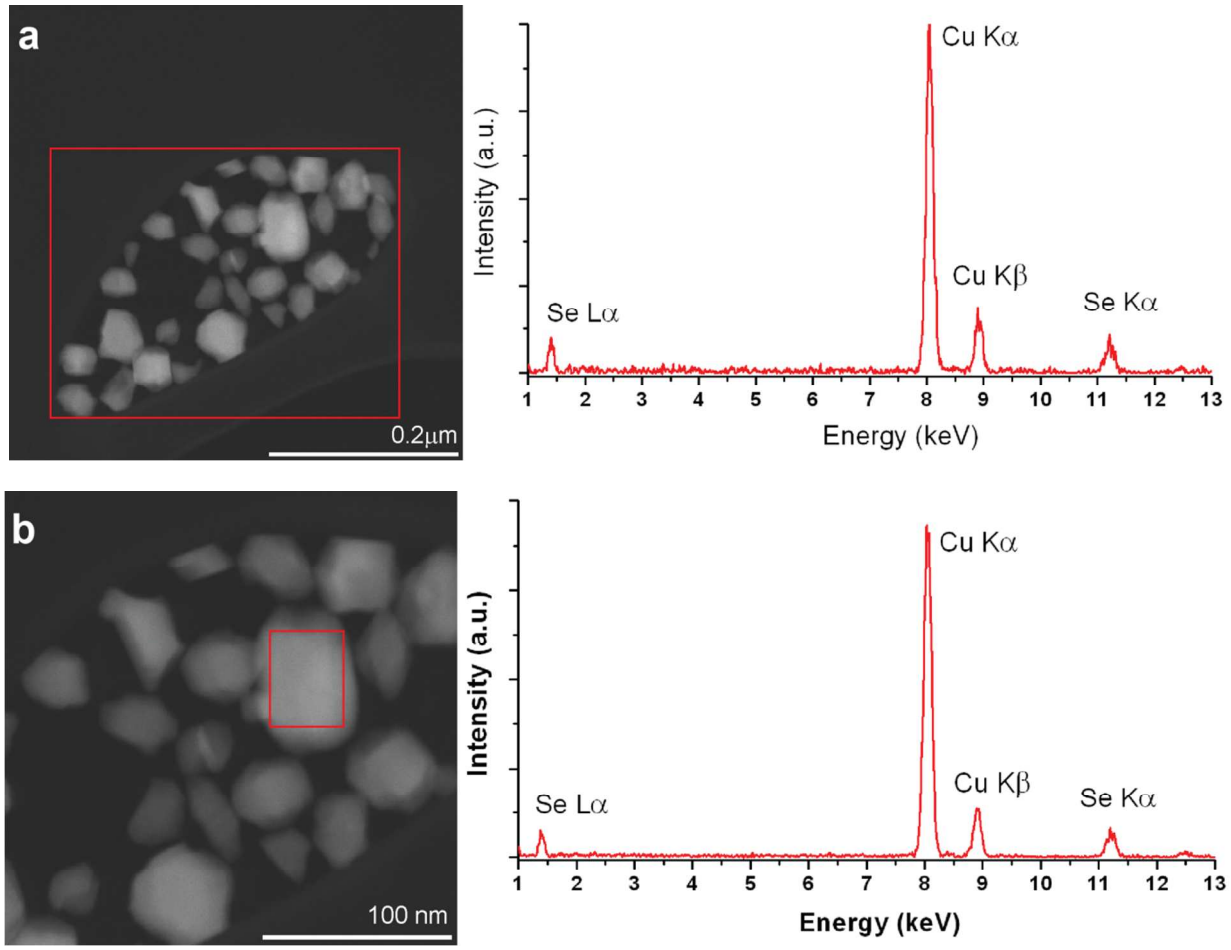

Figure S3. *STEM-EDX analyses performed on NCs after annealing experiment.* ***a)*** *Survey analysis of several NCs and the corresponding overall EDX spectrum where no Cd peaks are evident.* ***b)*** *Detail of a single NC and its corresponding EDX spectrum, here again no Cd peaks are detected. The red rectangles depict the scanned areas for elemental analysis.*

TEM annealing experiments

The thermal annealing treatment was also performed on the sole Cu_3P and CdSe NCs. In this case no destabilization or dissolution process was observed on the NCs, even after keeping the samples at a temperature of 450°C for more than 30 minutes, nor was observed any loss/sublimation of P and Cd atoms, as shown by EFTEM maps in Figure S4.

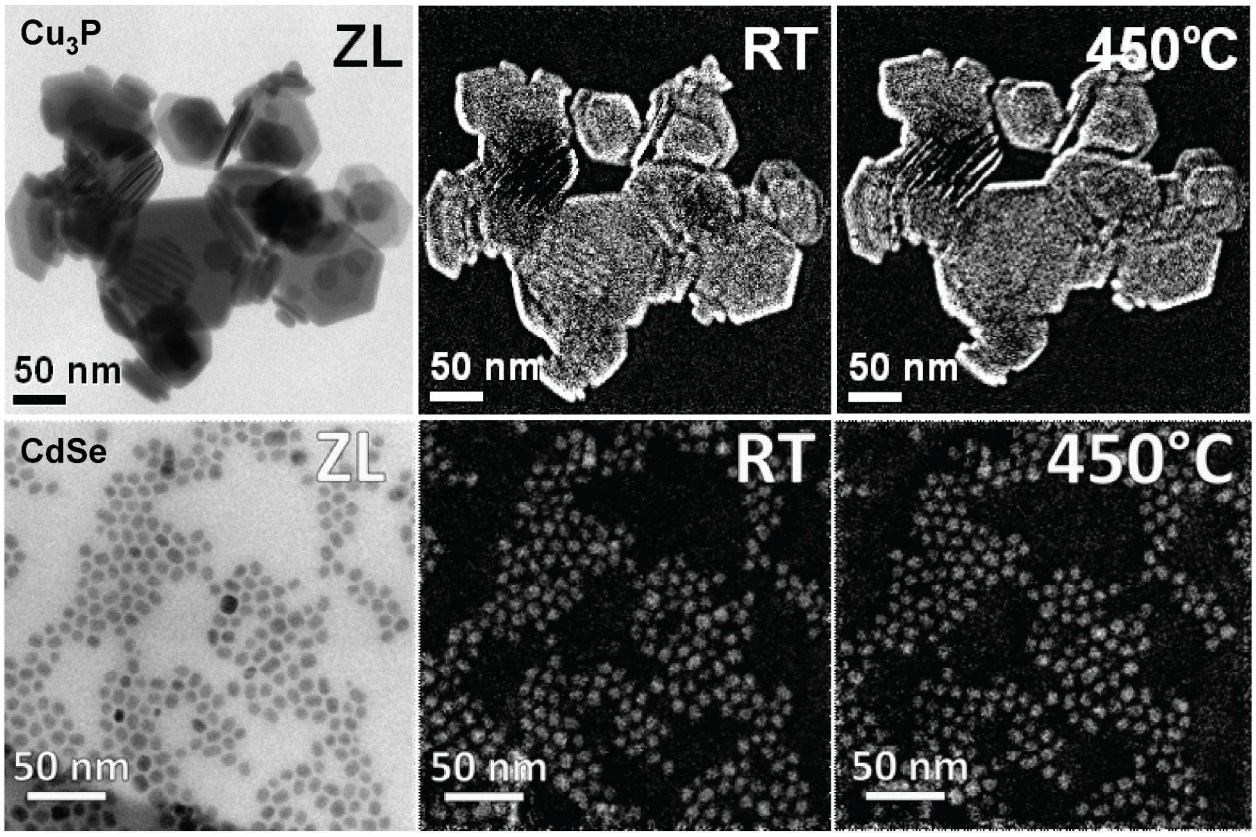

Figure S4. *Thermal treatment of sole Cu3P (upper row) and CdSe (lower row) NCs. Elastic filtered image (ZL) of several NCs recorded at room temperature (left), with elemental maps via EFTEM obtained by filtering the L-edge of P (132 eV) and M-edge of Cd (404 eV) for Cu3P and CdSe NCs, respectively, recorded at room temperature (center) and 450°(right).*

The same thermal annealing treatment was also performed on the CdSe/Cu_3P/CdSe nano-corals. In this case destabilization and dissolution process was observed on the NCs at a temperature of 500°-550° C. These values are a bit higher than the corresponding sandwich-like nanostructures. The cause could be ascribed to the presence of a residual organic shell covering the NCs that interfered with the ion diffusion and sublimation (Figure S5). As shown in the EFTEM maps a non-complete diffusion/sublimation of P and Cd occurred at 550° C. In any case, the signal of this element became blurry due to their diffusion and partial sublimation.

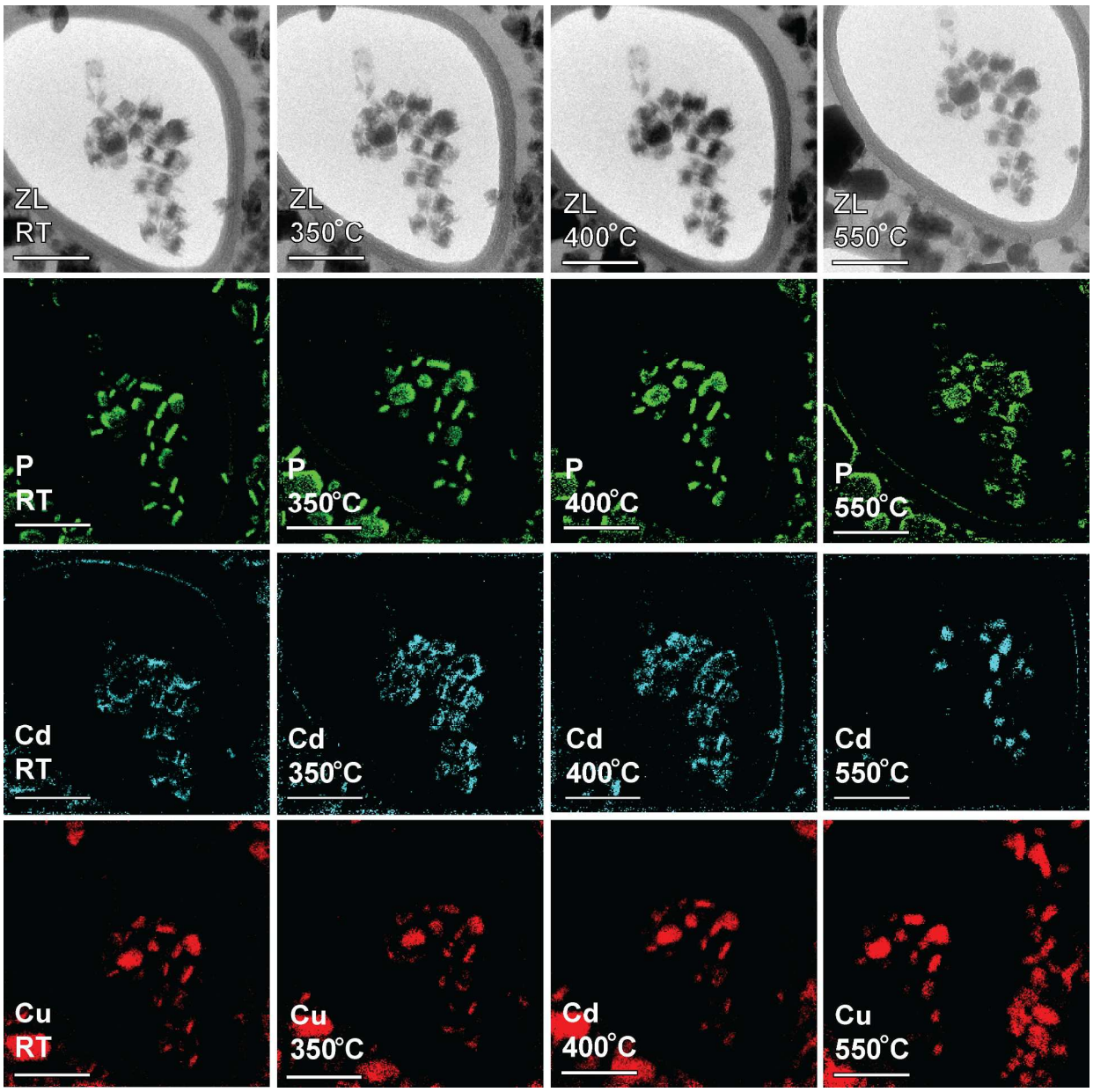

Figure S5. *Elastic filtered image (ZL) and EFTEM elemental maps of several CdSe/Cu_3P/CdSe nano-corals between room temperature (RT) and 550°C using an ultrathin Cu grid. Elemental maps were obtained by using the EELS L-edges of P (132eV, depicted in green,) Cd (404eV, depicted in cyan) and Cu (931 eV, depicted in red), respectively. All the scale bars reported correspond to a length of 100 nm.*