Supporting Information

Formation of colloidal copper indium sulfide nanosheets by two-dimensional self-organization

Anne C. Berends,[1] Johannes D. Meeldijk,[2] Marijn A. van Huis,[3] and Celso de Mello Donega[1]*

[1] Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands

[2] Electron Microscopy Utrecht, Utrecht University, 3584 CH Utrecht, The Netherlands

[3] Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands

*Corresponding author. E-mail: c.demello-donega@uu.nl

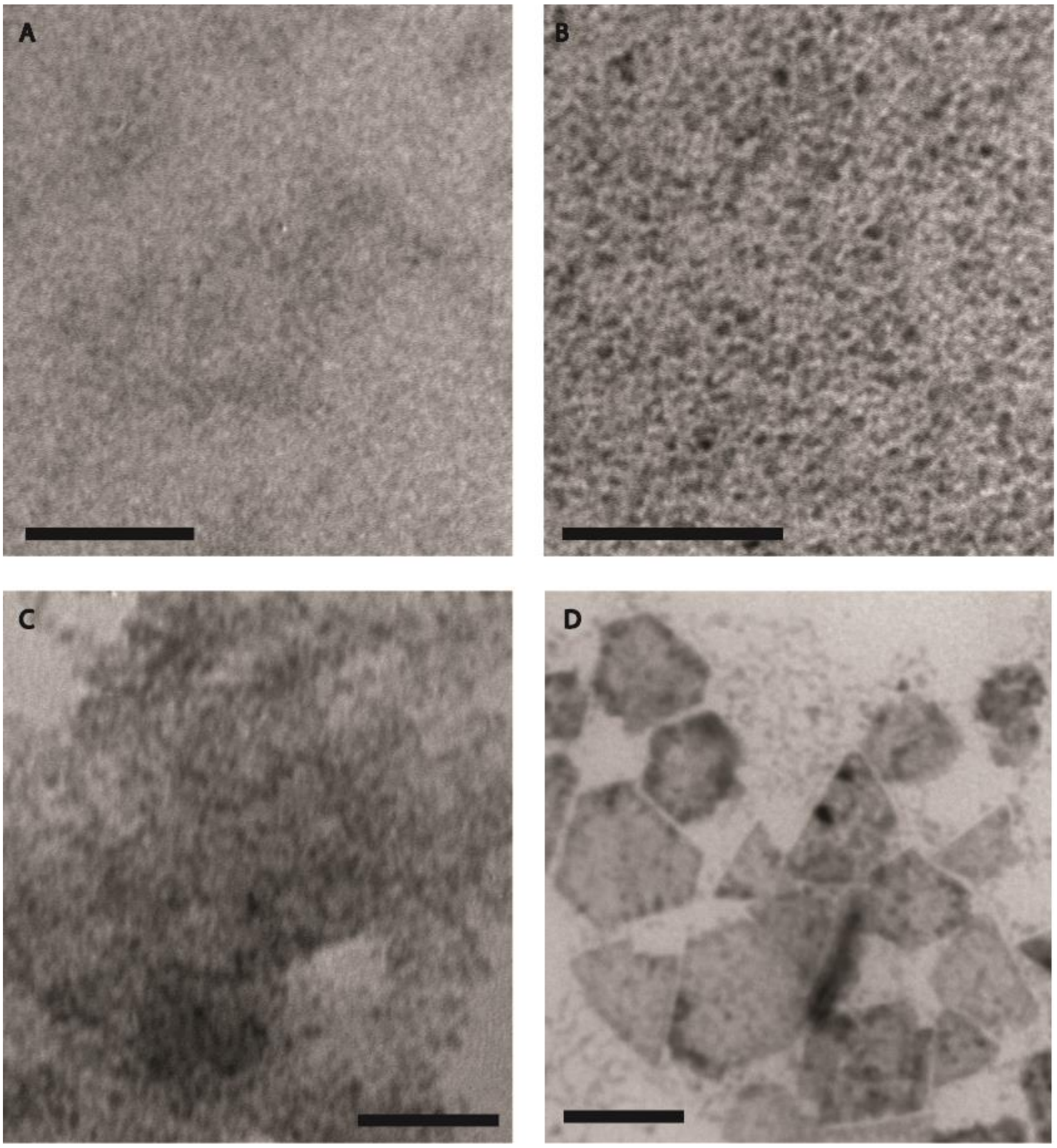

Figure S1. TEM images of product nanocrystals obtained after control reactions at 200 °C for 2 hours. The CIS NC seeds were the same in all cases (dodecanethiol capped chalcopyrite trigonal pyramidal NCs with a height of 2.5 nm). **(A)** CIS NCs in ODE. **(B)** CIS NCs in ODE and oleylamine. **(C)** CIS NCs in a solution of sulfur in ODE. **(D)** CIS NCs in a solution of sulfur in ODE and octadecylamine. All scale bars correspond to 50 nm.

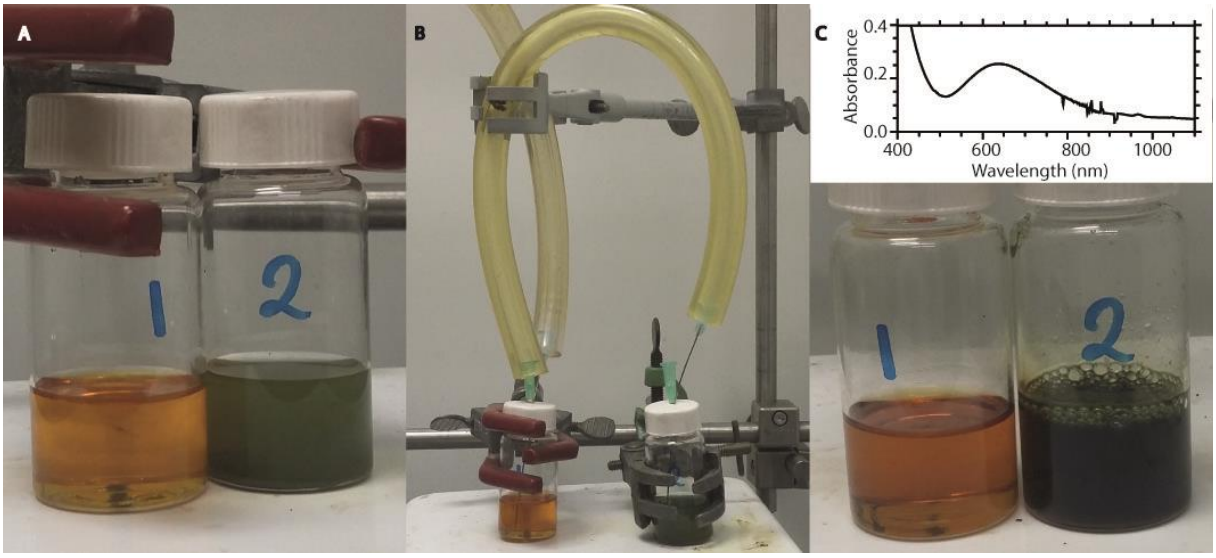

Figure S2. ***In situ* formation of H_2S. (A)** In vial 1 (orange solution), oleylamine and elemental sulfur are dissolved in ODE. In vial 2 (green solution), Cu(I)acetate is dissolved in oleylamine. **(B)** The vials are connected and a nitrogen flow from vial 1 to 2 is established. The vials are heated to 200 °C under a constant nitrogen flow. **(C)** After a few minutes the color of the solution in vial 2 changes from green to black. The absorption spectrum of the mixture in vial 2 after reaction is shown in the inset. This spectrum is very similar to that of small $Cu_{2-x}S$ NCs, showing that a product formed in vial 1 reacted with Cu(I) ions in vial 2 to produce $Cu_{2-x}S$ NCs. This product can be identified as H_2S, since the reaction between sulfur and alkylamines at high temperatures is known to produce a number of compounds (alkylammonium polysulfides, alkylthioamides, dialkylamidines, alkyl-thioketoamidines, H_2S),[1] of which only H_2S is a gas at the reaction conditions.

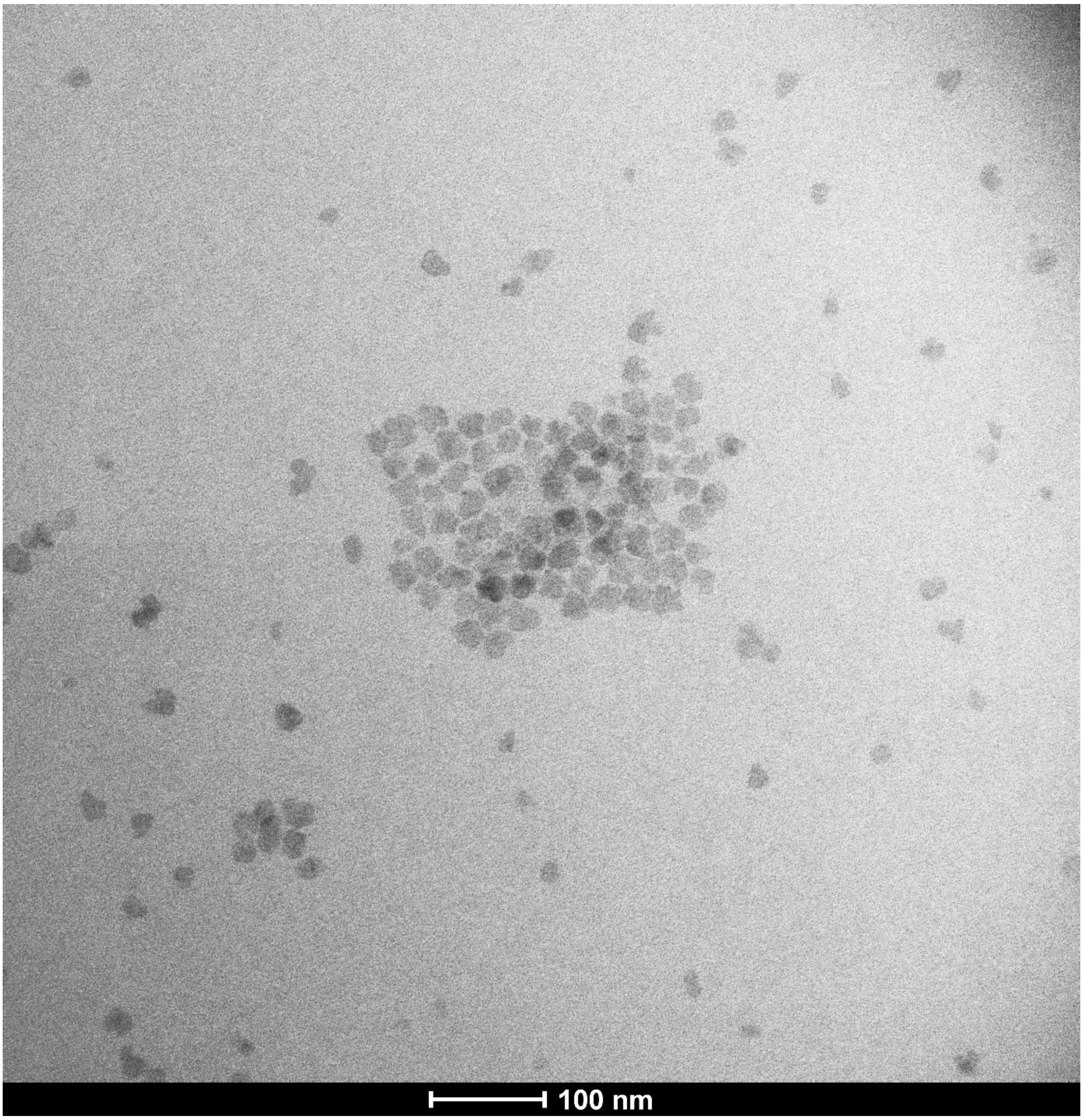

Figure S3. TEM image of product nanosheets obtained from 2.5 nm CIS NC seeds in OLAM and S-ODE after 1 minute reaction at 80 °C.

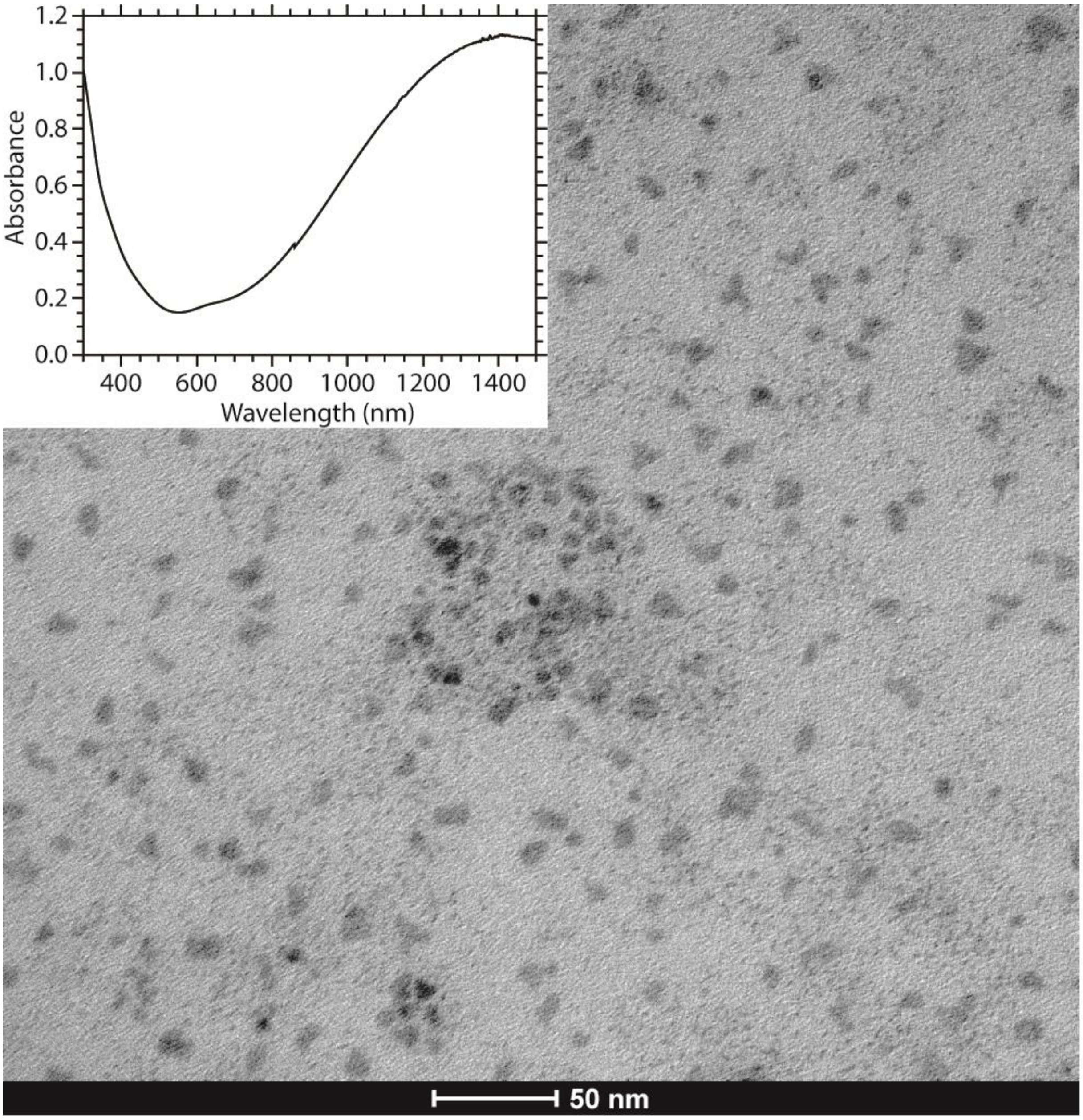

Figure S4. TEM image of product nanocrystals obtained from 2.5 nm CIS NC seeds in OLAM and S-ODE after 3 days at RT. Inset shows the absorption spectrum of the sample.

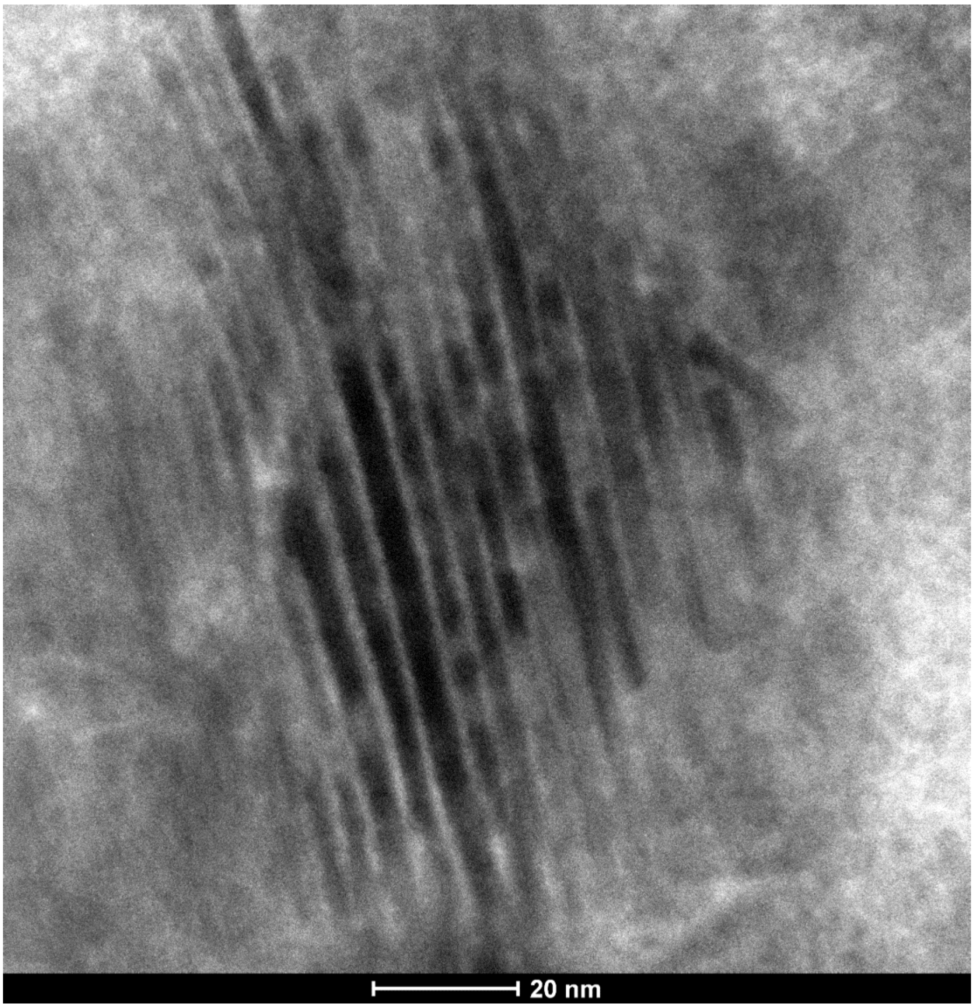

Figure S5. TEM image of stacked nanosheets, allowing the determination of their thickness (3-4 nm).

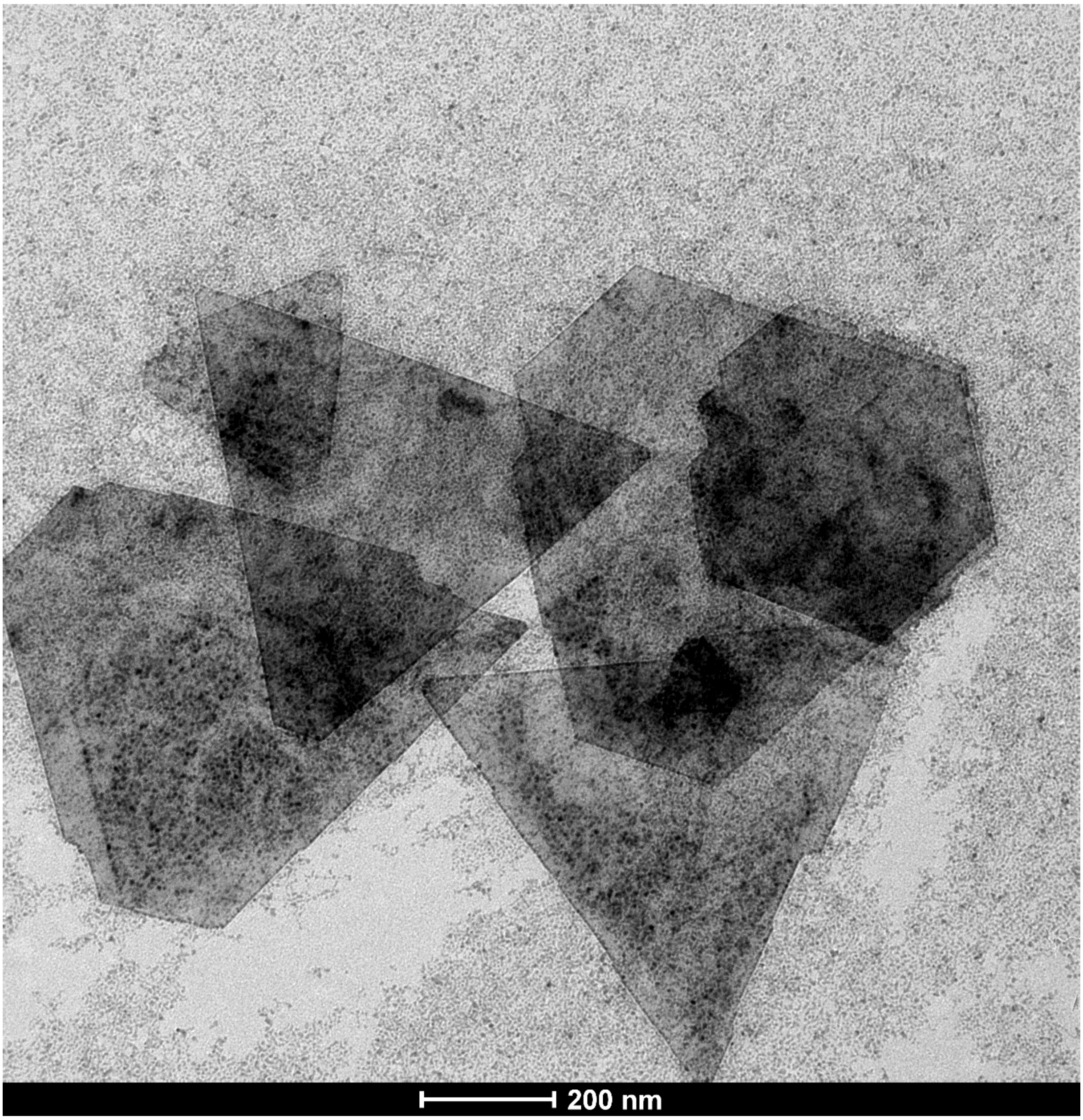

Figure S6. TEM image of NSs and small particles on the background and adsorbed on the surfaces of the NSs. The size of the small particles is estimated to range from 4 to 11 nm.

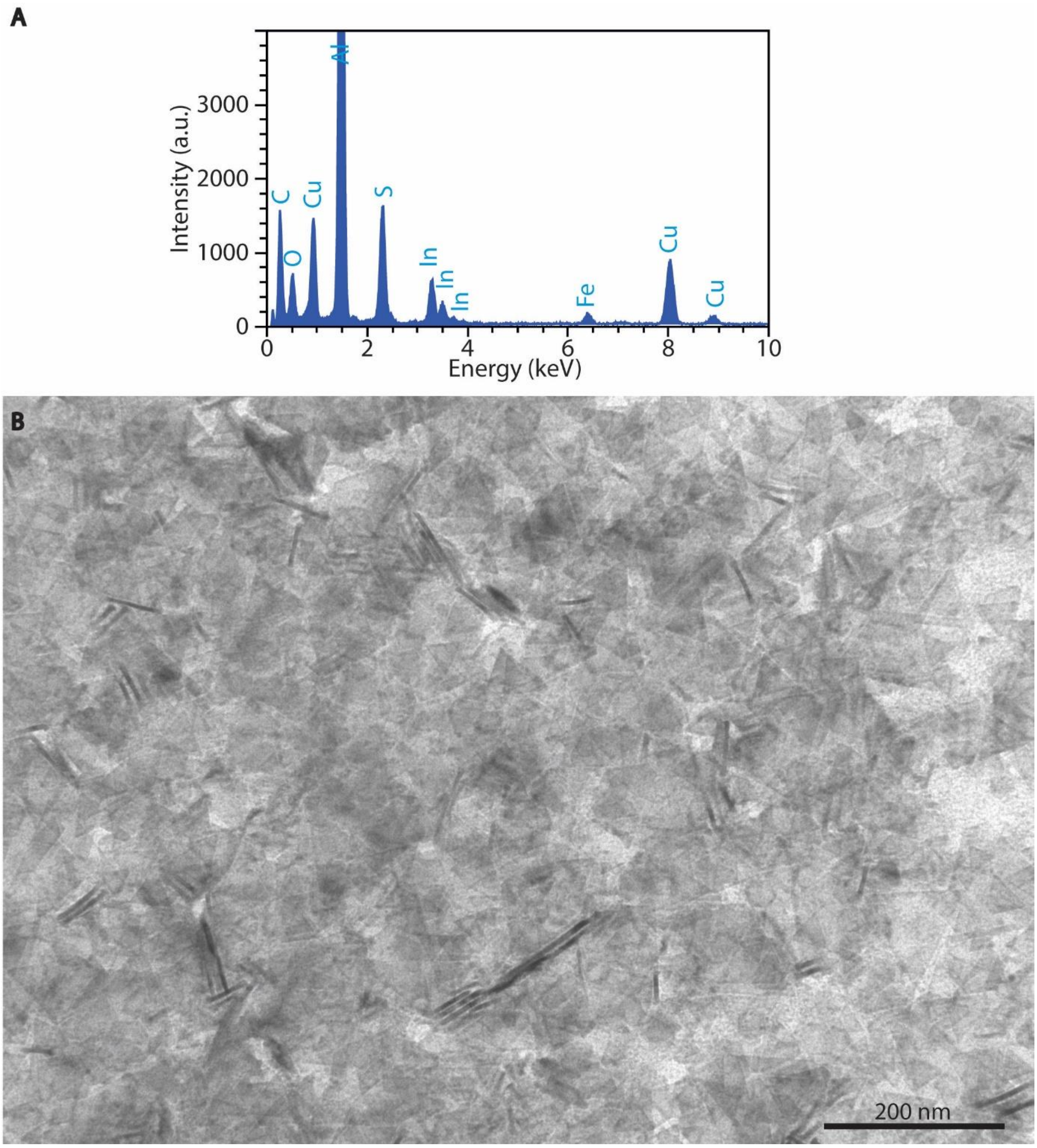

Figure S7. **(A)** Representative EDX spectrum of product NSs obtained from parent CIS NCs. The assignment of the peaks is indicated in the figure. Aluminum TEM grids were used in order to measure indium, copper and sulfur ratios without interference of the grid-material. In these grids, traces of iron are present as well. The TEM image of the area used to collect the EDX spectrum is shown in **(B)**

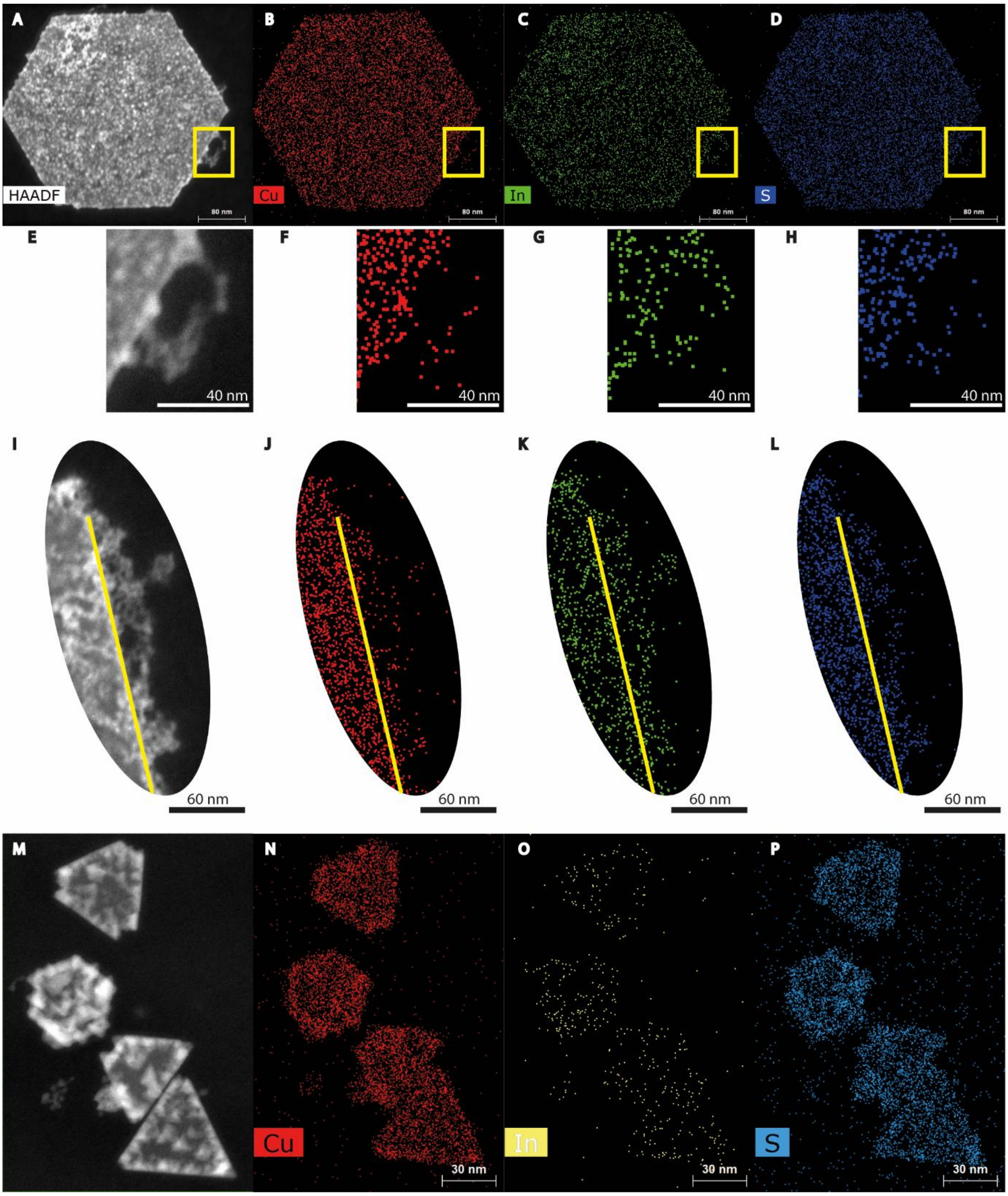

Figure S8. EDX elemental maps of product NSs obtained from parent CIS NCs. The yellow frame in Figures A-D highlights an area with isolated small particles that appear to be indium rich, as this area is clearer in the indium map than in the copper map. A zoom-in of this area is shown in Figures E-H. The Figures I-L are a zoom-in of Figure 3 from the main text. The maps were acquired over a constant measuring time. This results in lower counts for areas with more bare grid (M-P compared to A-D).

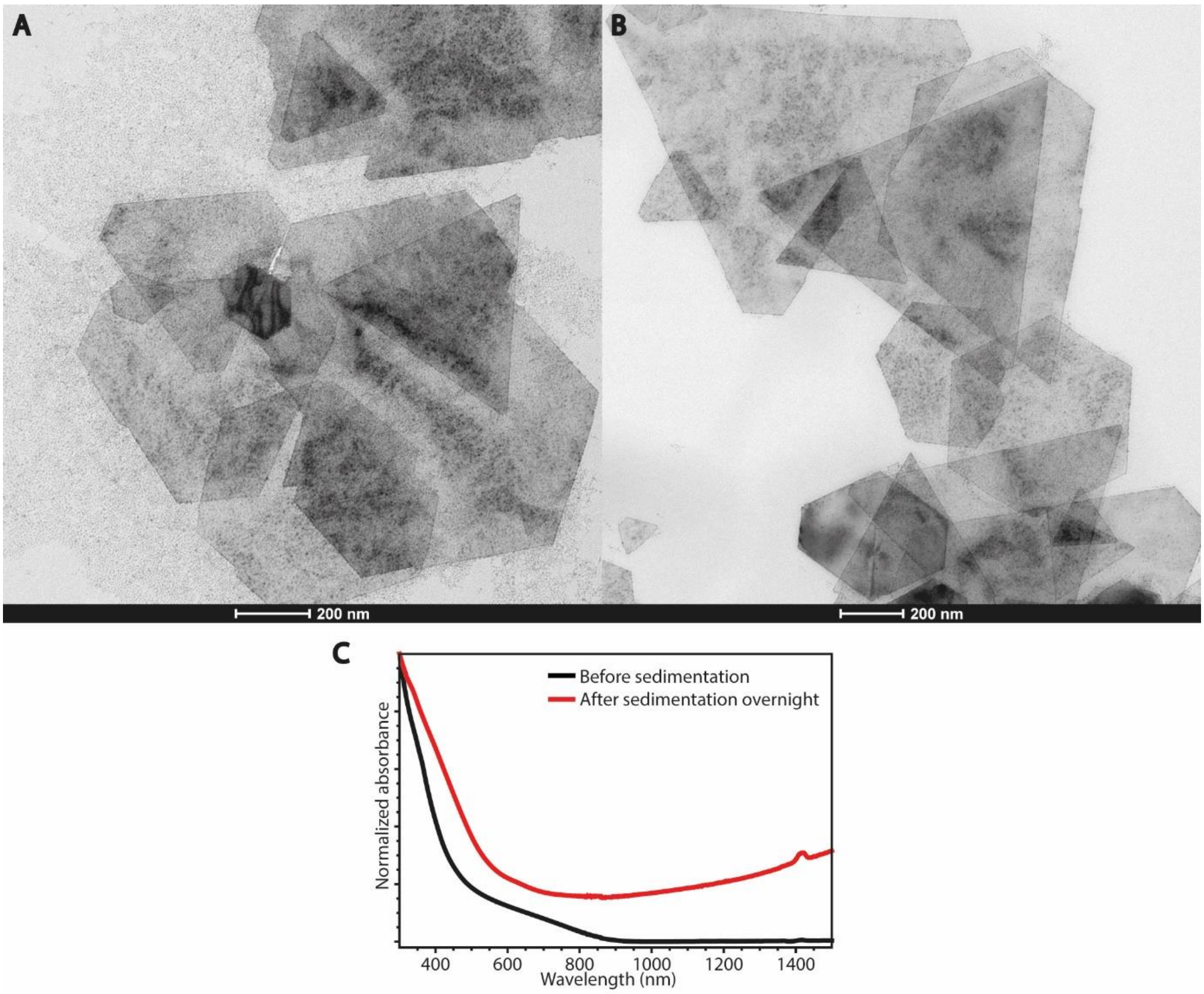

Figure S9. (A) TEM image of product NCs obtained from 2.5 nm CIS NC seeds in OLAM and S-ODE after 2 h at 200 °C prior to purification by sedimentation. **(B)** TEM image of the sediment obtained from the sample shown in (A). **(C)** Absorption spectra of sample containing NSs and small particles (black) and after sedimentation of the NSs (red).

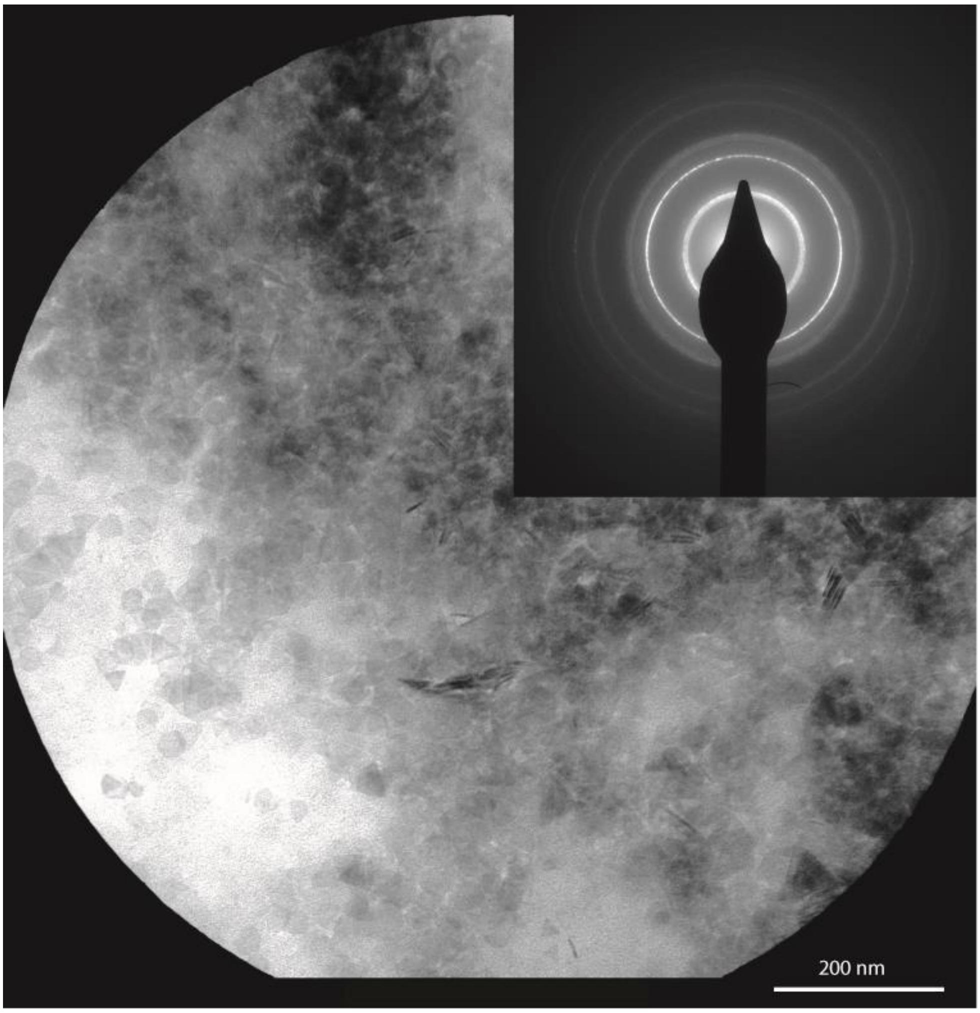

Figure S10. Selected area showing a batch of deposited CIS nanosheets. The electron diffraction (ED) pattern of this batch is shown in the inset. The azimuthally integrated ED pattern is shown in Figure 5b of the main text.

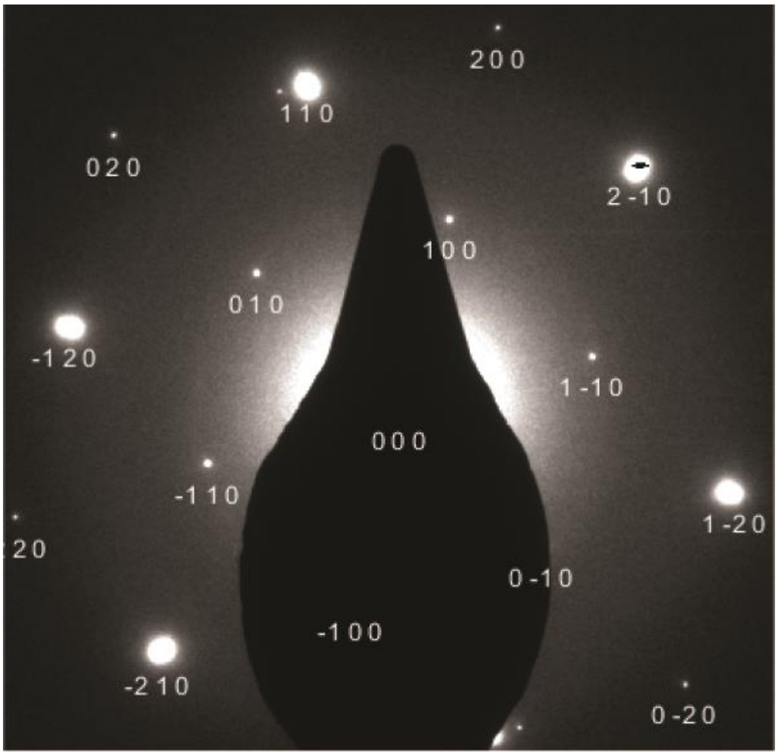

Figure S11. Electron diffraction pattern of a single nanosheet, shown in Figure 5 of the main text. The ED spots are assigned to covellite lattice planes.

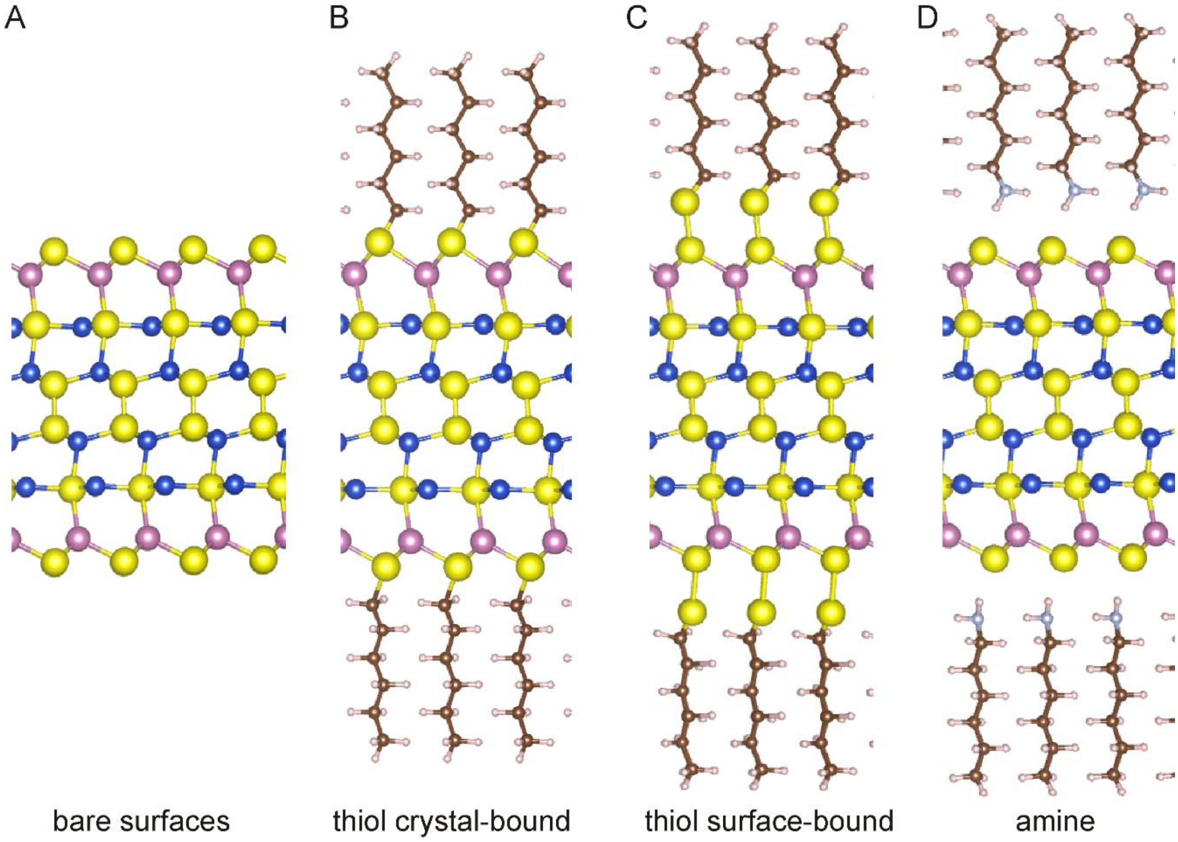

Figure S12. Bare and ligand-covered 6-bilayer covellite structures evaluated by DFT-OptB88-vdW simulations. (A) bare (B) crystal-bound thiol-covered, (C) surface-bound thiol-covered, and (D) amine-covered slabs. The supercells used are periodic and 58 Å in height, containing a vacuum slab at least 22 Å thick; in width 3-4 supercells are displayed. Cu, In and S atoms are displayed as blue, magenta, and yellow spheres, respectively. C, N, and H atoms are displayed in brown, cyan and white colors, respectively. The 2D covellite slab displayed in (A) was fully relaxed (dimensions and atomic coordinates) using OptB88-vdW, after which the lateral cell dimensions were kept fixed for evaluation of the ligand coverage (B-D) using OptB88-vdW while allowing full relaxation of atomic coordinates.

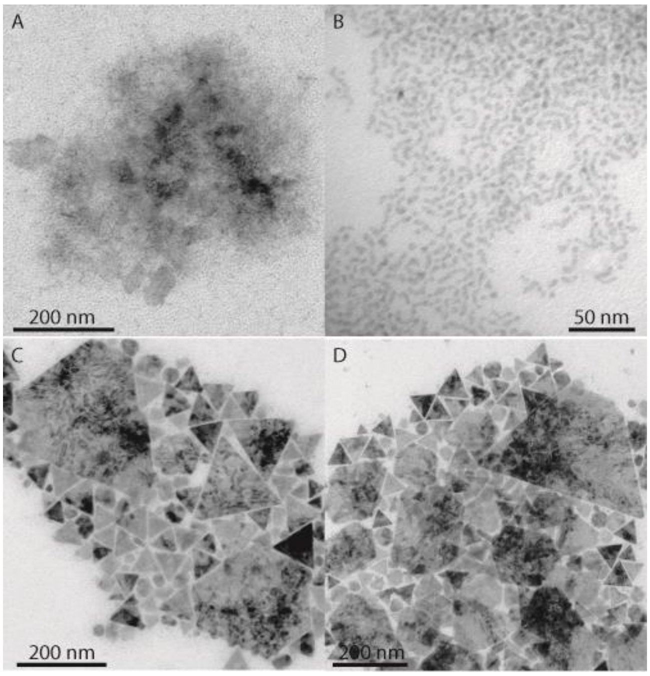

Figure S13. Product NCs obtained by following the same synthesis protocol used to obtain CIS nanosheets, but with addition of (A) $InCl_3$, (B) $InCl_3$ and $ZnCl_2$, (C) ammonium bromide and (D) ammonium chloride. Addition of metal cations to the reaction mixture clearly prevents the formation of nanosheets, while ammonium cations and halide anions do not.

References

[1] Thomson, J. W.; Nagashima, K.; Macdonald, P. M.; Ozin, G. A. From Sulfur-Amine Solutions to Metal Sulfide Nanocrystals: Peering into the Oleylamine- Sulfur Black Box. J. Am. Chem. Soc. 2011, 133, 5036–5040.