Electronic Supplementary Information

Ternary Hybrid Nanostructures of Au-CdS-ZnO Grown *via* a Solution-Liquid-Solid Route Using Au-ZnO Catalysts

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Experimental Details:

1. Materials

Zinc acetate (99.99%), gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), sulfur (S, 99.98%), octadecylamine (90%), 1,2-hexadecanediol (90%), and oleylamine (70%) were purchased from Sigma Aldrich. Benzyl alcohol (99%) and octadecene (90%) were purchased from Alfa Aesar. Cadmium acetylacetonate ($Cd(acac)_2$, 98%) and trioctylphosphine (TOP, 97%) were purchased from Strem. All chemicals were used as received.

2. Synthesis of Au-ZnO Nanorods

Au-ZnO nanorods were synthesized according to a previously published protocol (see reference 27 in the article) with some modifications. In a 4 mL vial, 20 mg $HAuCl_4 \cdot 3H_2O$ was weighed and then dissolved in 3.5 mL benzyl alcohol with the aid of sonication. The resulted gold solution was transferred to a 25 mL three-neck-round bottom flask, equipped with a magnetic stir bar, together with 92 mg zinc acetate, 2.457 g octadecylamine, and 2.5 mL octadecene. Then, the three necks of the flask were sealed with rubber septa and the flask was purged with nitrogen for 15 min, at room temperature, under stirring (the stirring was maintained throughout the entire procedure). After the purging period the nitrogen inlet and outlet needles were taken out and the mixture was heated to 120 °C. After 20 min incubation at this temperature, the mixture was heated to 190 °C where it was held for 30 min before cooling it to room temperature. The product solution was

divided equally between three 15 mL centrifuge tubes, 7 mL hexane and 2 mL ethanol were added to each tube and the tubes were heated for several minutes in a hot water bath to prevent the octadecylamine solidification. Then, the tubes were centrifuged for 10 min and the red precipitate in each tube was redispersed in 7 ml hexane. 1 mL oleylamine was added to the hexane solution in each tube and the tubes were sonicated for ~15 min until a clear solution was obtained (this step was essential for getting a stable colloidal solution). After the sonication period, each tube was added 6 mL ethanol and was centrifuged for 10 min. The precipitate was dissolved in hexane to create a stock solution. The stock solution concentration was evaluated by optical absorbance so that a stock solution diluted by a factor of 15 would give absorbance of ~0.7 at the ZnO absorption shoulder (the location of this shoulder was at ~355 nm in most of the syntheses).

3. Synthesis of Au-CdS-ZnO Hybrid Nanostructures

The Au-CdS-ZnO hybrid nanostructures were synthesized by the following procedure: first, 0.2 mL of TOP-Cd stock solution (prepared by dissolving 9.5 mg $Cd(acac)_2$ in 1 mL TOP) was mixed with 0.2 mL of TOP-S stock solution (prepared by dissolving 1.0 mg S in 1 mL TOP) in a 4 mL vial with a septum cap. In another septum capped 4 mL vial, 15 mg 1,2-hexadecanediol was added to 0.6 mL TOP. The two mixtures were prepared under inert environment inside a glovebox. Then, 0.35 mL of Au-ZnO stock solution (see previous section for details) and 3 mL oleylamine were added to a 25 mL three-neck-round bottom flask, equipped with a stir bar and connected to a standard Schlenk line, and the solution was stirred and heated to 320 °C under nitrogen. At that point, the TOP solution of the 1,2-hexadecanediol (pre-heated at ~60 °C, until the moment of injection, to dissolve the hexadecanediol) was rapidly injected to the Au-ZnO solution, followed immediately by a dropwise injection of the TOP-(Cd, S) solution. The solution was incubated at 320 °C for 30 min (this time was measured from the end of the precursors' injection) before rapidly cooling it to room temperature by immersion of the flask in a water bath. The product solution was transferred to a 15 mL centrifuge tube, ~1 mL hexane and ~6 mL ethanol were added and the tube was centrifuged for 10 min. The brown precipitate was redispersed in ~1 ml hexane, ~3 mL ethanol was added, and the tube was centrifuged once more for 10 min.

The product was redispersed in hexane and was saved for further characterization.

4. Characterization Methods

Transmission electron microscopy (TEM) images were obtained by a Tecnai 12 TWIN (FEI) microscope operated at 120 kV. High resolution TEM (HRTEM), and scanning TEM (STEM) images together with energy dispersive X-ray spectroscopy (EDS) were obtained by a JEOL TEM 2100-F microscope operated at 200 kV. X-ray diffraction (XRD) data was collected using PANalytical Empyrean powder diffractometer equipped with position sensitive (PSD) X'Celerator detector using Cu Kα radiation (λ=1.5418 Å) and operated at 40 kV and 30 mA. UV-Vis absorbance spectra were taken by a Cary 5000 and JASCO V-550 UV-vis-NIR spectrophotometers.

5. ICSD card numbers for the bulk XRD patterns in Fig. 2b and S2

Cubic Au – card No. 00-004-0784

Wurtzite ZnO – card No. 00-076-0704

Wurtzite CdS – card No. 00-075-1545

hcp Au_2Cd (α_2) – card No. 00-005-0683

Hexagonal AuCd (β'') – card No. 00-065-2046

Cubic AuCd (β) – card No. 00-065-0434

Figures:

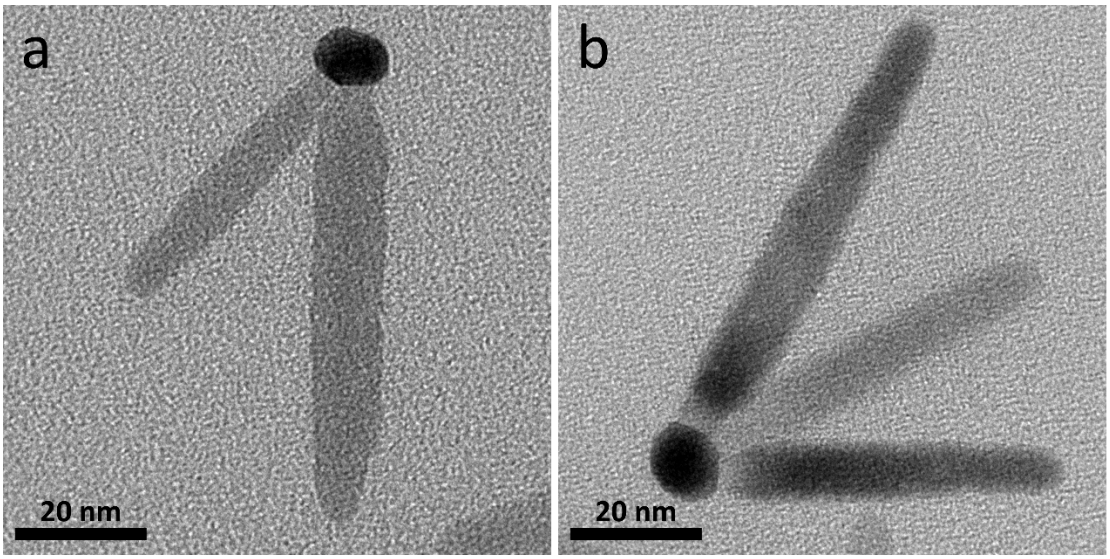


Fig. S1 TEM images of Au-ZnO hybrid bipods (a) and tripods (b).

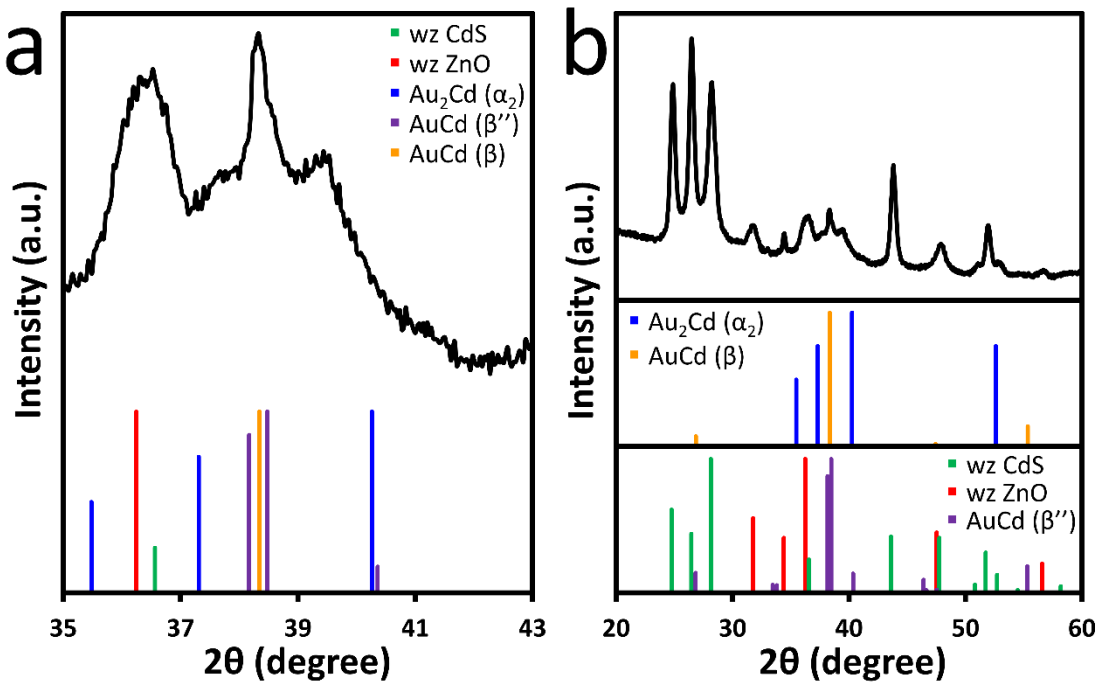


Fig. S2 The Au-CdS-ZnO XRD pattern shown in Figure 2b together with the bulk patterns of hcp Au_2Cd (α_2), hexagonal AuCd (β''), and cubic AuCd (β) (in addition to the bulk patterns of wurtzite CdS and wurtzite ZnO). (a) A magnified section of the pattern between 35° and 43°; (b) The same pattern in the region between 20° to 60°.

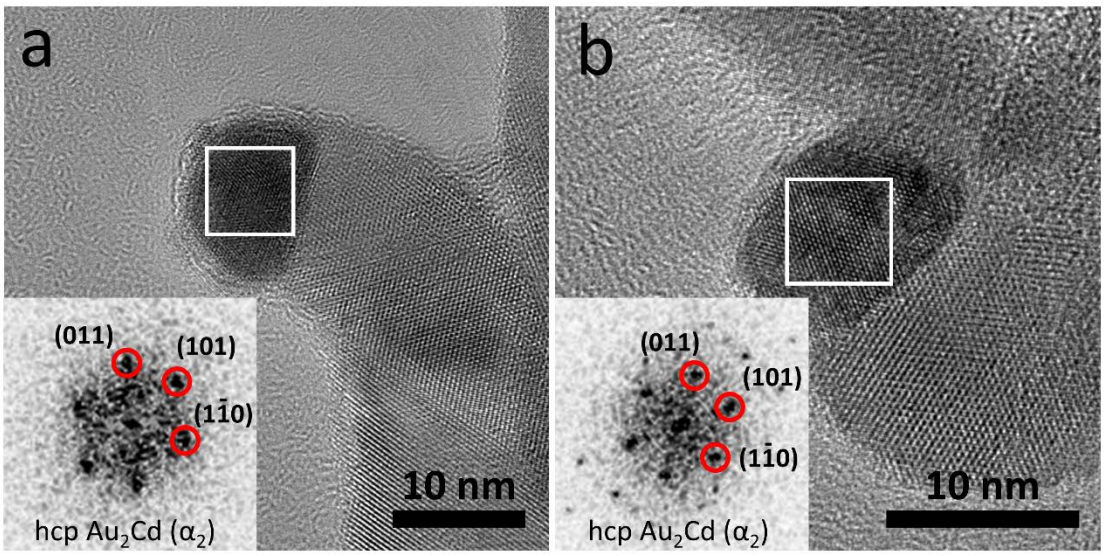


Fig. S3 HRTEM images of different Au-CdS-ZnO hybrid nanostructures together with FFT images of the square areas at the metal tips (shown in the inset of each image).

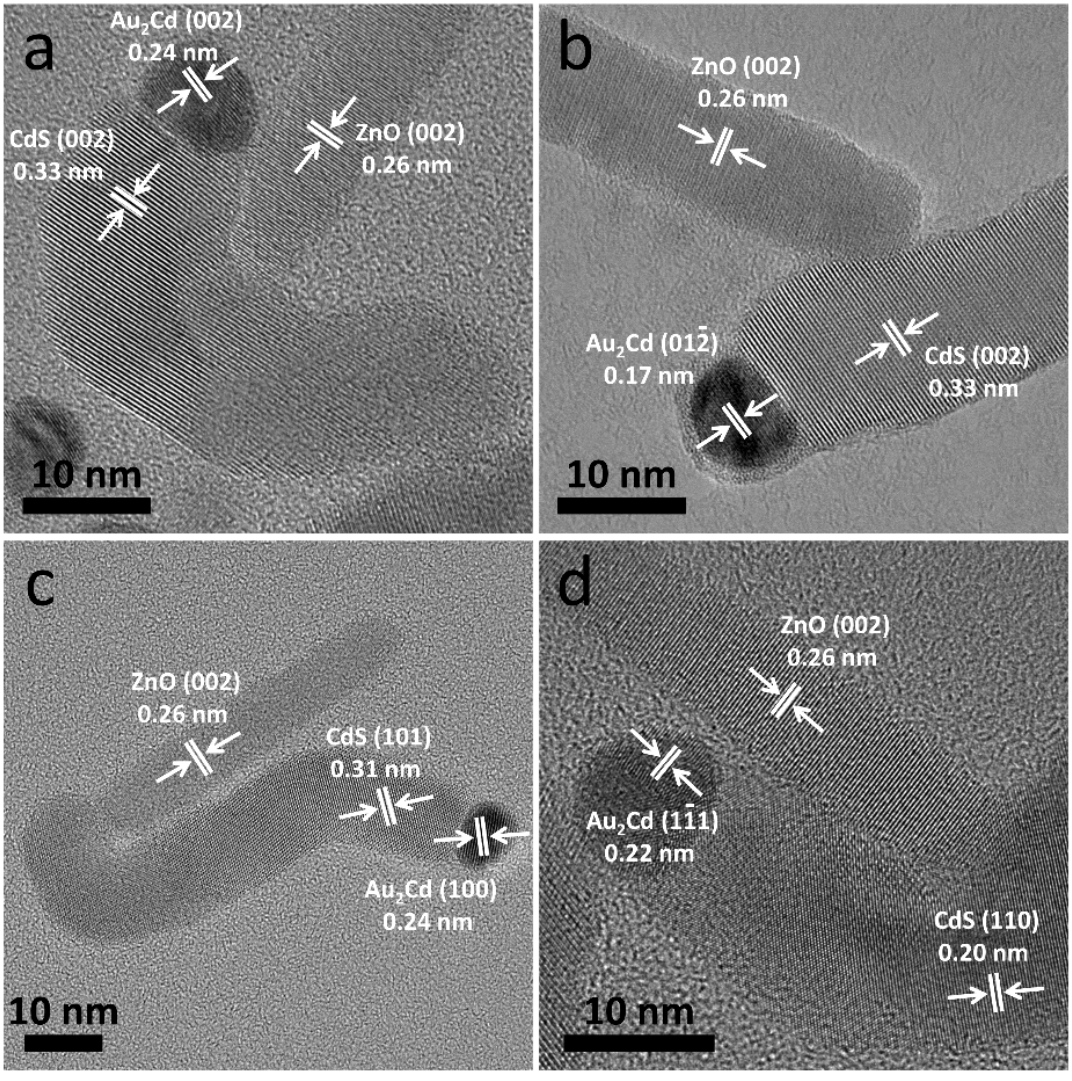


Fig. S4 HRTEM images of various Au-CdS-ZnO hybrid nanostructures.

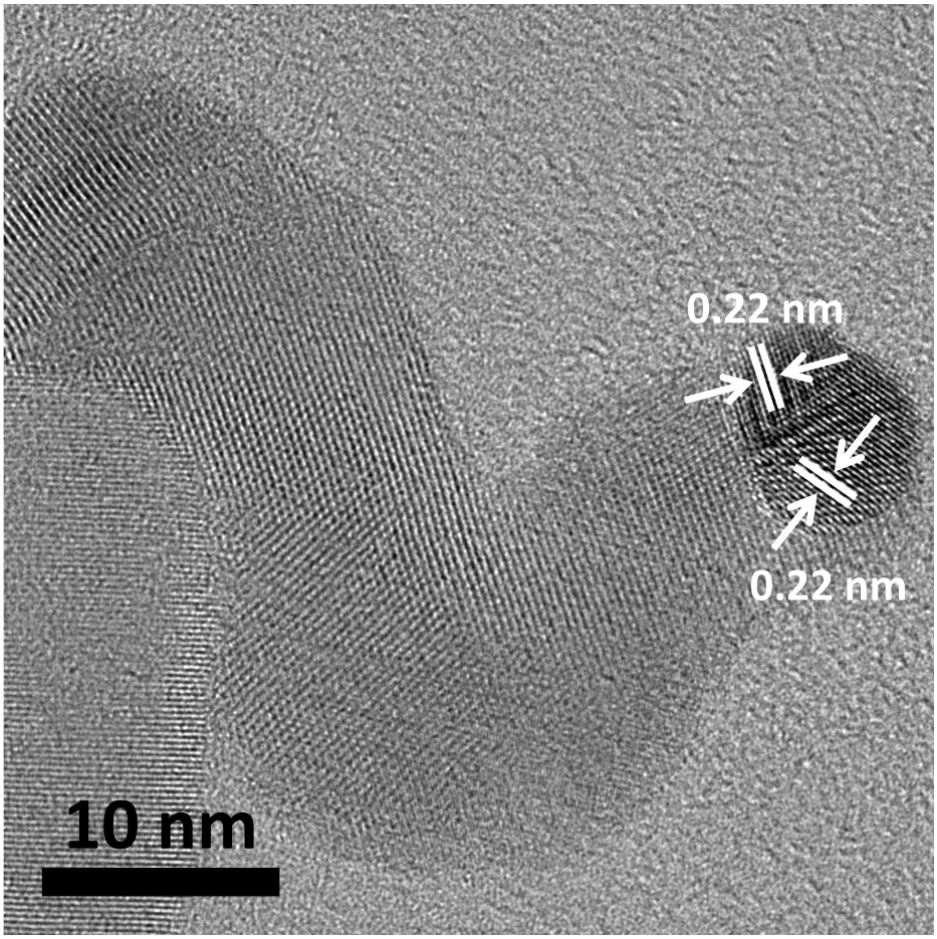


Fig. S5 HRTEM image of Au-CdS-ZnO hybrid nanostructure with a polycrystalline tip.

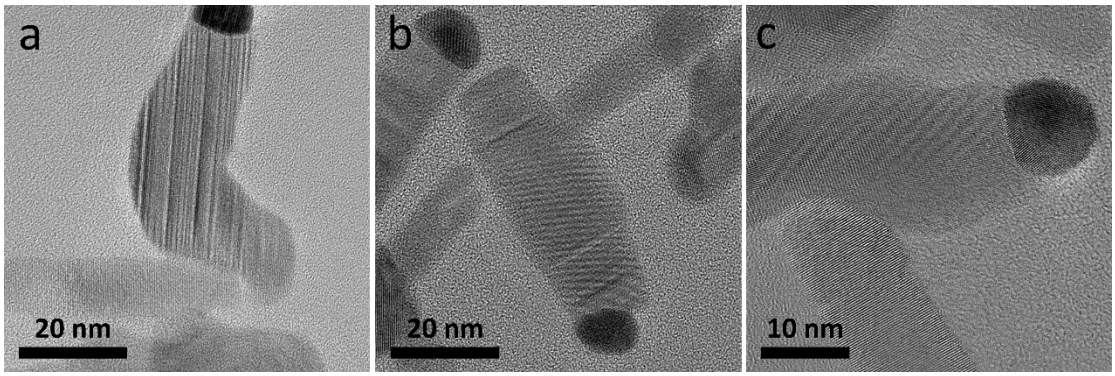
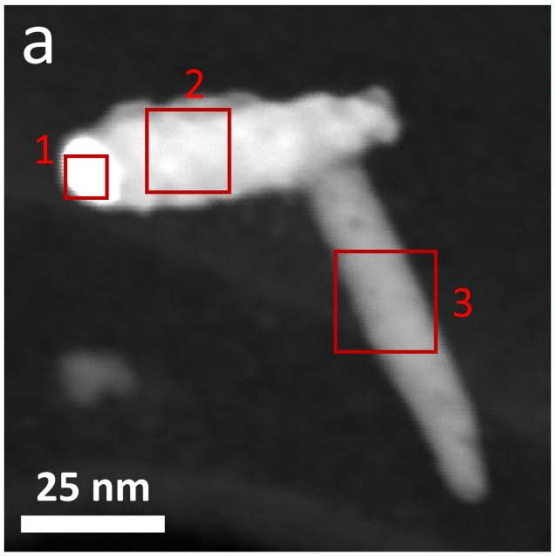
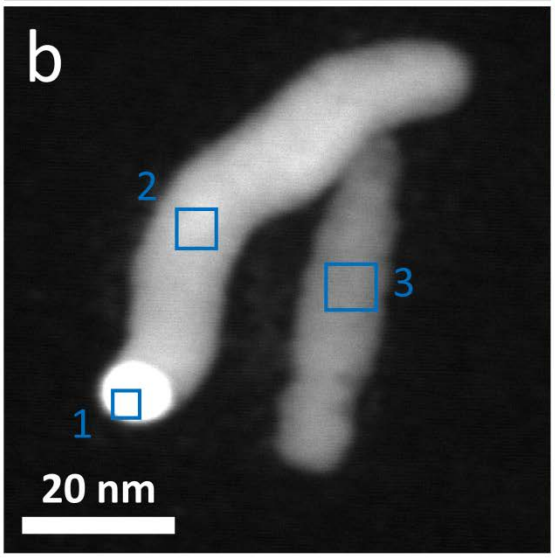


Fig. S6 HRTEM images of Au-CdS-ZnO hybrid nanostructures with planar defects in the CdS domain.



Region / Element	1 (atomic %)	2 (atomic %)	3 (atomic %)
Au	28.2	0.0	0.0
Cd	28.8	36.0	0.0
S	0.0	24.9	0.0
Zn	3.5	0.6	31.9
O	39.5	38.5	68.1



Region / Element	1 (atomic %)	2 (atomic %)	3 (atomic %)
Au	47.0	2.3	0.0
Cd	22.3	44.9	0.0
S	5.0	44.1	0.0
Zn	4.3	2.9	53.2
O	21.4	5.8	46.8

Fig. S7 Dark field STEM images of representative Au-CdS-ZnO hybrid nanostructures (left), and tables that summarize the results of the EDS composition analysis in each of the squares shown in the corresponding STEM images (right).