

Annealing of sulfide stabilized colloidal semiconductor nanocrystals

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Supporting Information

Synthesis of colloidal nanocrystals

Chemicals

$\text{Cu}(\text{acac})_2$ (Aldrich, 99,99%), $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (Aldrich, 99,999%), SnCl_4 (Aldrich, 98%), Se (Alfa Aesar, 99,999%), Oleylamine (Acros, Tech. 80-90%), 1-Octadecene (Alfa Aesar, Tech. 90%).

$\text{Cu}_2\text{ZnSnSe}_4$ (Fig S1 a-c)

- 1.35 mmol $\text{Cu}(\text{acac})_2$, 1.6 mmol $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and 0.75 mmol SnCl_4 are combined with 10 ml oleylamine in a three-neck flask
- Flask is attached to a Schlenk line and flushed with nitrogen for 1h during stirring at room temperature
- Meanwhile, 2.975 mmol Se is dispersed in 2 ml of oleylamine and stirred at room temperature
- The flask containing the cations is heated to 250°C, after which the Se-oleylamine mixture is rapidly injected
- The mixture is allowed to react for 15 min at 240°C
- Reaction is cooled down using a water bath
- Toluene and ethanol are added to wash the NCs
- The precipitant collected after centrifugation is redissolved in toluene
- 2 additional washing steps are carried out right before layer deposition or ligand exchange

CdSe (Synthesis according to Jasieniak et al¹, Fig S3 a-c)

Characterization of CIS NCs capped by ammonium sulfide

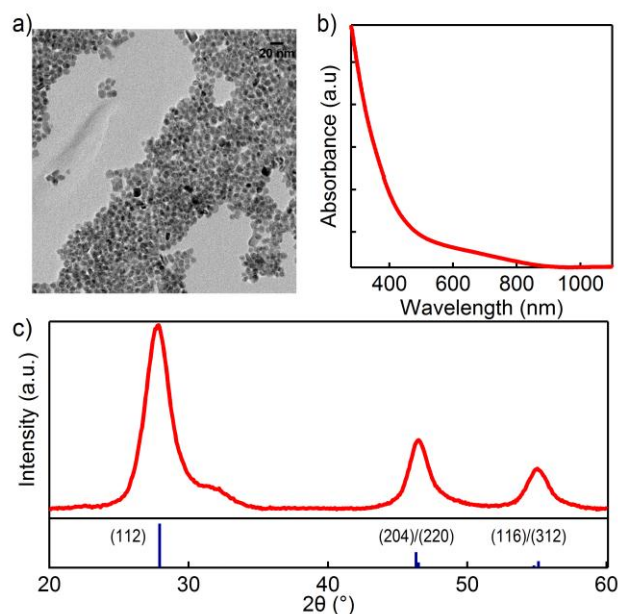


Fig. S1 Characterization of CIS NCs after ligand exchange to $(\text{NH}_4)_2\text{S}$. (a) TEM image. (b) UV-VIS-NIR spectrum of a NC solution. (c) XRD pattern of a NC thin film.

Characterization of CZTSe and CdSe NCs

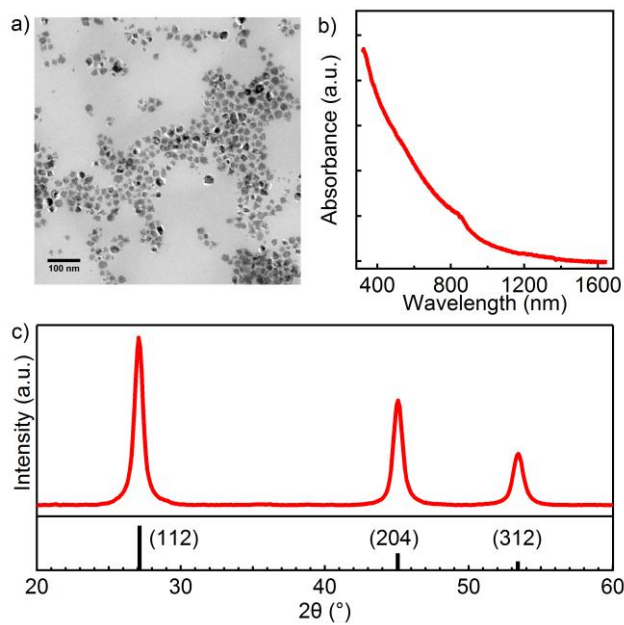


Fig. S2 Characterization of CZTSe NCs. (a) TEM image. (b) UV-VIS-NIR spectrum of a NC solution. (c) XRD pattern of a NC thin film.

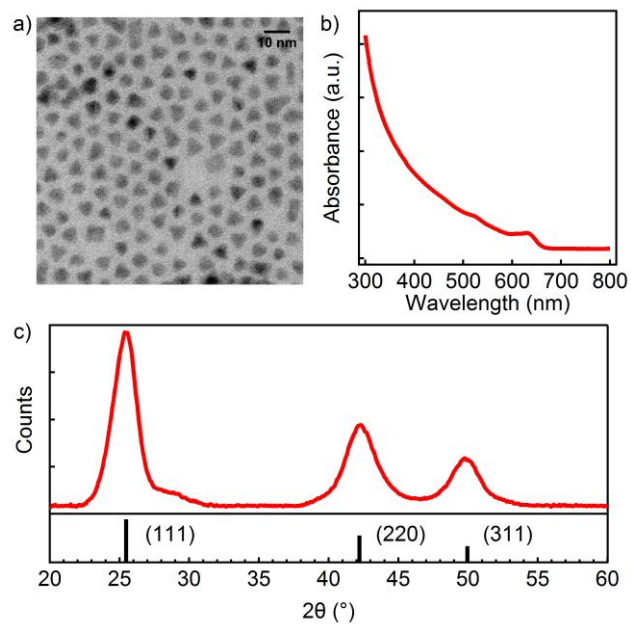


Fig. S3 Characterization of CdSe NCs. (a) TEM image. (b) UV-VIS spectrum of a NC solution. (c) XRD pattern of a NC thin film.

Annealing of CZTSe and CdSe NCs stabilized by $(\text{NH}_4)_2\text{S}$

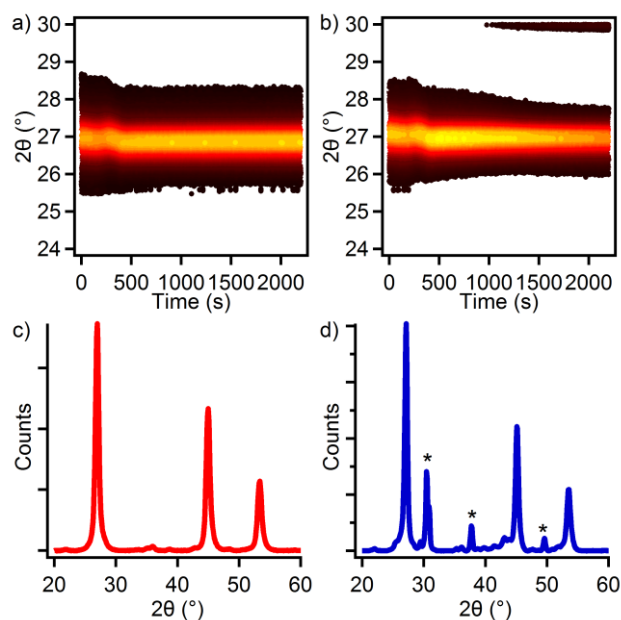


Fig. S4 Comparison of annealing behavior of CZTSe NCs capped with $(\text{NH}_4)_2\text{S}$. (a-b) In-situ XRDs following the (112) peak during the heating process in helium respectively forming gas. (c-d) Pattern taken after the thermal treatment in helium (c) and forming gas (d). (*) Indicate the formation of the binary phase SnSe, as observed in the upper right part of (b).

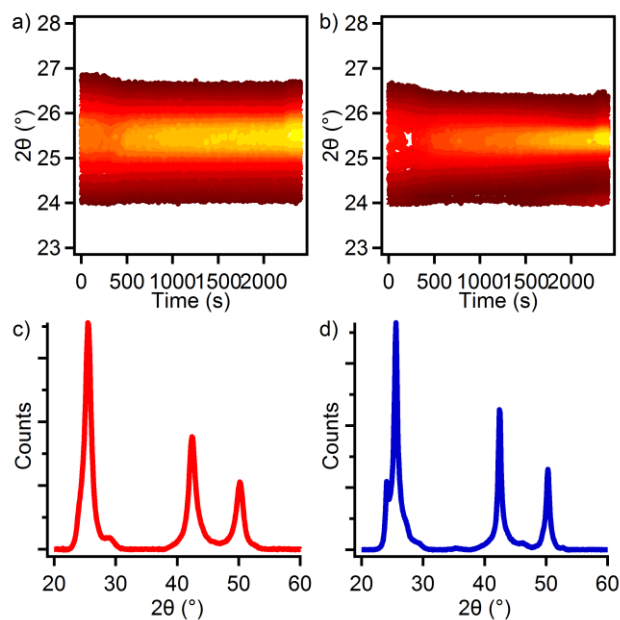


Fig. S5 Comparison of annealing behavior of CdSe NCs capped with $(\text{NH}_4)_2\text{S}$. (a-b) In-situ XRDs following the (112) peak during the heating process in helium respectively forming gas. (c-d) Pattern taken after the thermal treatment in helium (c) and forming gas (d).

Scherrer analysis

	CuInS_2				$\text{Cu}_2\text{ZnSnSe}_4$			CdSe		
	Synth.	Ann. He	Ann. He	Ann. H_2	Synth.	Ann. He	Ann. H_2	Synth.	Ann. He	Ann. H_2
Ligand	Oleylamine	Oleylamine	$(\text{NH}_4)_2\text{S}$	$(\text{NH}_4)_2\text{S}$	Oleylamine	$(\text{NH}_4)_2\text{S}$	$(\text{NH}_4)_2\text{S}$	Oleic acid	$(\text{NH}_4)_2\text{S}$	$(\text{NH}_4)_2\text{S}$
Peak position ($^\circ$)	27,9	27,9	27,9	27,9	27,0	27,0	27,2	25,5	25,5	25,6
Crystallite size (nm)	4,0	8,2	5,7	14,6	11,7	12,9	16,5	4,0	6,8	11,7

Table S1 Peak positions for the (112) peak and corresponding crystallite sizes calculated using the Scherrer formula (shape factor=0,9). Synth. = Pattern from as-synthesized NCs. Ann.He/ H_2 = Pattern from NC thin films annealed in helium/forming gas.

References

- (1) Jasieniak, J., Bullen, C., van Embden, J., & Mulvaney, P. (2005). Phosphine-free synthesis of CdSe nanocrystals. *Jour. Phys. Chem. B*, 109(44), 20665–20668