

## SUPPORTING INFORMATION FOR

# Size Control and Quantum Confinement in $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystals

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### SYNTHETIC PROCEDURES:

**Chemicals:** Copper (II) chloride dihydrate (ACS grade, 99+%), tin (IV) chloride pentahydrate (98%), zinc chloride (reagent grade, 98%), sodium diethyldithiocarbamate trihydrate (ACS grade), oleylamine (technical grade, 70%), oleic acid (technical grade, 90%), 1-octadecene (technical grade, 90%), chloroform (HPLC grade,  $\geq 99.8\%$ ), and toluene (HPLC grade, 99.9%) were purchased from Sigma-Aldrich. Hexane (ACS grade) was purchased from VWR International. Reagent alcohol (histological grade, 90% ethyl alcohol, 5% methyl alcohol, 5% butyl alcohol) was obtained from Fisher Scientific. All chemicals were used as delivered without further purification. Ultra-high purity water (18 M $\Omega$ ) was obtained from a Millipore Direct-Q water purification system.

**Synthesis of Copper Diethyldithiocarbamate [ $\text{Cu}(\text{dedc})_2$ ]:** 9.0 g of sodium diethyldithiocarbamate was dissolved in 150 mL of reagent alcohol and added dropwise to a solution of 4.23 g of copper chloride in 50 mL reagent alcohol (85 mg/mL) with constant stirring. The black precipitate that formed upon reaction was filtered and washed multiple times with ultra-high purity water before drying in a desiccator.  $\text{Cu}(\text{dedc})_2$  crystals were purified by recrystallization from chloroform and dried overnight in vacuum before use. The crystals melted at 200 °C.

**Synthesis of Zinc Diethyldithiocarbamate [ $\text{Zn}(\text{dedc})_2$ ]:** 9.0 g of sodium diethyldithiocarbamate was dissolved in 150 mL of reagent alcohol and added dropwise to a solution of 3.38 g of zinc chloride in 50 mL of reagent alcohol (68 mg/mL) with constant stirring. The white precipitate that formed upon reaction was filtered and washed multiple times with ultra-high purity water before drying in a desiccator.  $\text{Zn}(\text{dedc})_2$  crystals were purified by recrystallization from chloroform and dried overnight in vacuum before use. The crystals melted at 181 °C.

**Synthesis of Tin Diethyldithiocarbamate [ $\text{Sn}(\text{dedc})_4$ ]:** 12.85 g of sodium diethyldithiocarbamate was dissolved in 200 mL of reagent alcohol and added dropwise to a

solution of 2.5 g of tin tetrachloride in 50 mL of reagent alcohol (50 mg/mL) with constant stirring. The orange precipitate that formed upon reaction was filtered and washed multiple times with ultra-high purity water before drying in a desiccator. This product was then dissolved in chloroform and filtered again to remove impurities. The chloroform was evaporated to obtain an orange crystalline powder of Sn(dedc)<sub>4</sub>, which melted at 156 °C.

**Synthesis of CZTS Nanocrystals:** The CZTS nanocrystals were synthesized under dry nitrogen gas using a Schlenk line. In a typical synthesis, 18 mL of octadecene and 2 mL of oleic acid were mixed in a 100 mL three-neck flask. 27 mg of Cu(dedc)<sub>2</sub>, 13.6 mg of Zn(dedc)<sub>2</sub>, and 26.7 mg of Sn(dedc)<sub>4</sub> were then added to this mixture and the flask was connected to the Schlenk line and degassed multiple times at 60 °C. The crystals dissolved on stirring to give a brown solution. The contents of the flask were heated to the synthesis temperature and a specific volume of oleylamine was injected into the mixture. The nanocrystal size was tuned by changing the temperature and the amount of oleylamine that was injected. For example, to synthesize nanocrystals with an average diameter of 2 nm, 3 mL of oleylamine was injected into the flask at 150 °C to initiate nucleation. The nanocrystals were then allowed to grow for 4 minutes before quenching the reaction by immersing the flask in water. For the synthesis of 2.5 nm nanocrystals, a mixture of 1.5 mL of oleylamine and 1.5 mL of octadecene were injected into the flask at 150 °C. For the synthesis of 5 and 7 nm CZTS nanocrystals, the injection was performed at 175 °C. To avoid premature decomposition of Sn(dedc)<sub>4</sub> at this temperature, Sn(dedc)<sub>4</sub> was not dissolved and heated in the reaction flask with the other complexes. Rather, Sn(dedc)<sub>4</sub> was dissolved in oleylamine and octadecene and injected into the flask. All other steps of the synthesis and purification steps remained the same. Specifically, for 5 nm nanocrystals, Sn(dedc)<sub>4</sub> was dissolved in a mixture of 1.5 mL of oleylamine and 1.5 mL of octadecene and injected into the flask at 175 °C. For 7 nm nanocrystals, Sn(dedc)<sub>4</sub> was dissolved in a mixture of 0.75 mL of oleylamine and 2.25 mL of octadecene and injected into the flask at 175 °C.

The nanocrystals were precipitated from the dispersion using reagent alcohol and were centrifuged for 5 minutes at 4000 rpm. The supernatant was discarded and the nanocrystals were redispersed in toluene. The precipitation and dispersion steps were repeated multiple times to remove excess oleylamine and oleic acid. Finally, the nanocrystals were dispersed in toluene and stored for later use.

#### CHARACTERIZATION DETAILS:

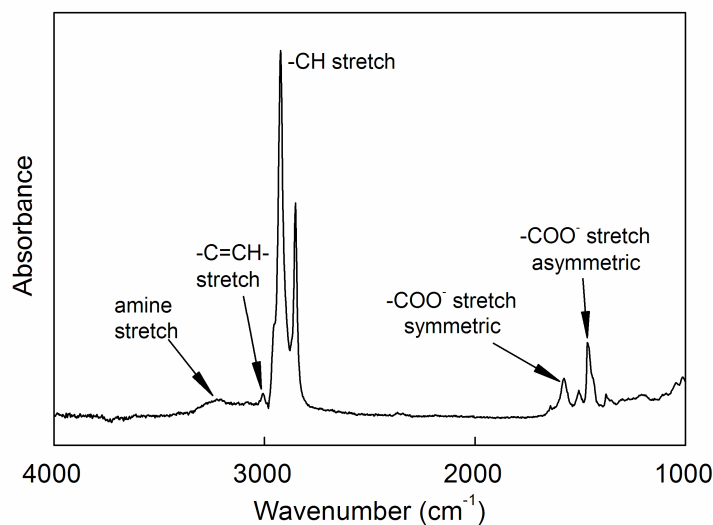
X-ray diffraction (XRD) patterns for the nanocrystals were collected and recorded using a Bruker-AXS microdiffractometer equipped with a Cu-K<sub>α</sub> X-ray source. The nanocrystals were examined and imaged using an FEI Tecnai G<sup>2</sup> F30 transmission electron microscope (TEM) with an acceleration potential of 300 kV. Optical absorbance spectra from nanocrystals dispersed in toluene was measured using a Cary 5 spectrophotometer. Pure toluene was used to obtain the background spectrum. For electron probe micro analysis (EPMA), we used a JEOL 8900R electron probe micro analyzer with an acceleration voltage of 10 kV, a beam current of 50 nA, and a beam diameter of 75 micrometers. Samples for electron probe micro analysis (EPMA) were prepared by drop casting a known volume of a dispersion of nanocrystals onto a silicon substrate to form a thin and uniform film. Raman measurements were carried out using a Witec confocal Raman microscope. The samples were excited using an Argon laser at 514.5 nm. The

Raman scattering signal was analyzed using a monochromator with a grating of 1800 lines/mm. Raman scattering was collected from thin films of nanocrystals that were cast on molybdenum-coated glass substrates from a dilute dispersion in toluene. Fourier transform infrared (FTIR) absorption spectra were collected using a Nicolet Magna 550 series II FTIR spectrophotometer with an attenuated total reflection (ATR) accessory (Harrick Scientific) and a Glowbar source. The infrared beam was focused normal onto the 45° beveled edge of the trapezoidal Ge ATR crystal ( $5 \times 1 \times 0.1 \text{ cm}^3$ ). Aliquots of colloidal CZTS suspensions were cast onto the Ge ATR crystal and allowed to dry before recording their FTIR spectrum.

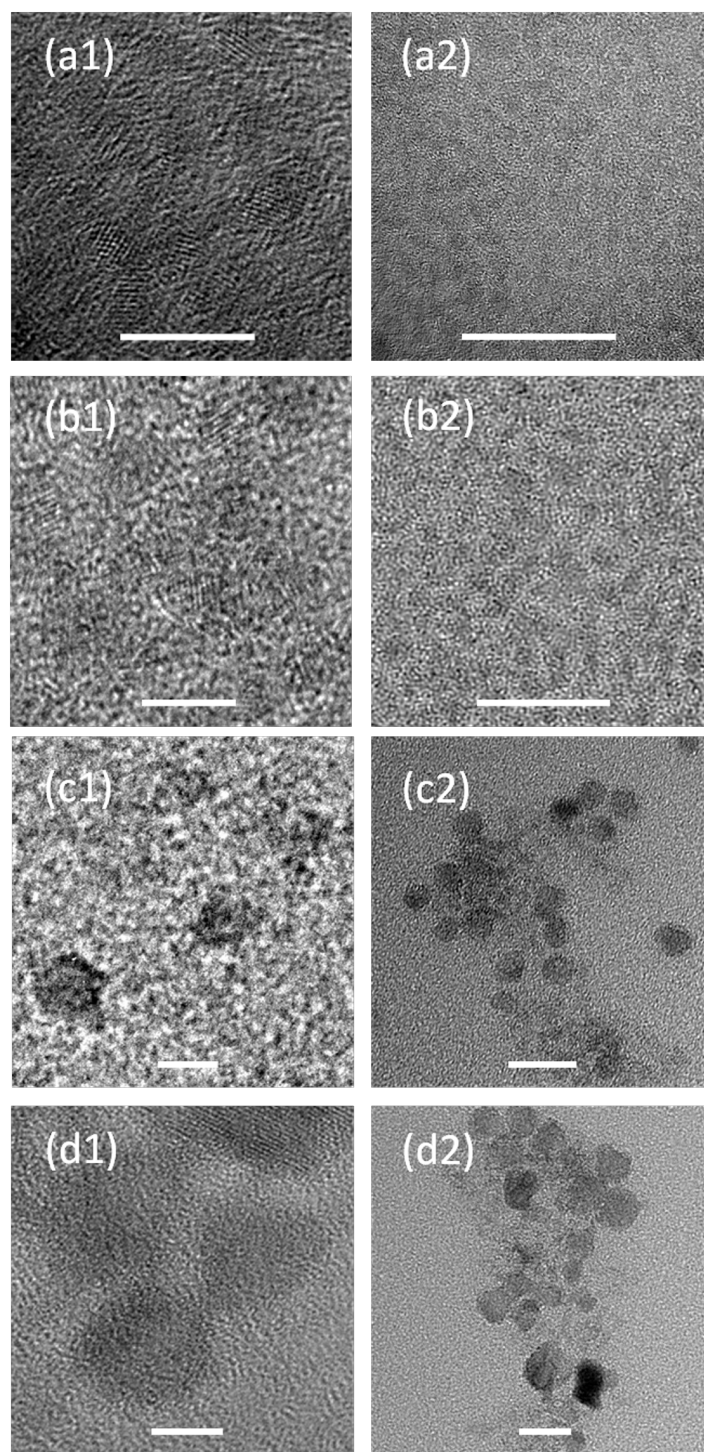
#### EPMA RESULTS:

Size	Zn/Cu	Sn/Cu	S/Cu
ideal	0.50	0.50	2.00
2 nm	0.53	0.58	2.83
2.5 nm	0.44	0.57	2.46
5 nm	0.49	0.54	2.36
7 nm	0.51	0.52	2.30

**Table SI-1** Elemental analysis data for our CZTS samples obtained using EPMA as a function of the average diameter of the nanocrystals. The elemental data has been reported after normalizing it to the amount of copper within the sample.

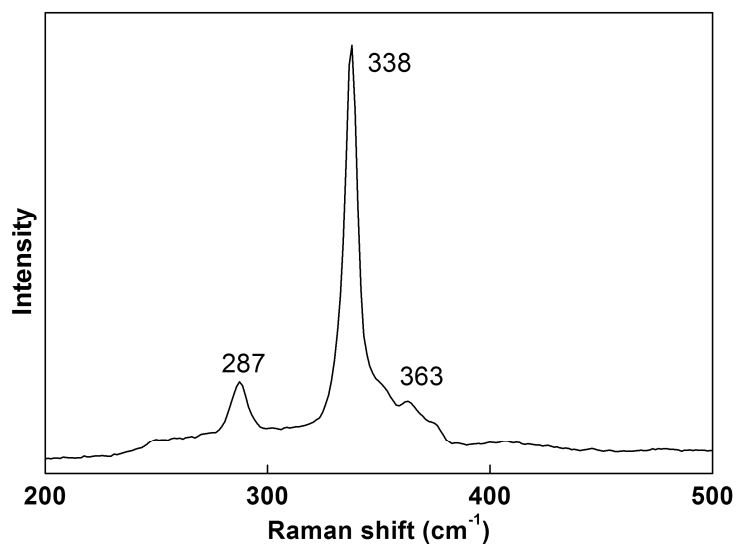


**Figure SI-1** FTIR spectra from CZTS nanocrystals. The FTIR data suggests that both oleylamine and oleic acid act as capping ligands for the nanocrystals.



**Figure SI-2** Low magnification TEM images of CZTS nanocrystals with average diameters of: a) 2 nm, b) 2.5 nm, c) 5 nm, and d) 7 nm. Scale bars for a1, b1, c1, and d1 are 5 nm. Scale bars for a2, b2, c2, and d2 are 20 nm.





**Figure SI-3** Raman spectra from thin films of CZTS nanocrystals annealed at 550 °C. The Raman peaks match those for bulk CZTS.