Supporting Information for

# Size and shape controlled hydrothermal synthesis of kesterite $Cu_2ZnSnS_4$ nanocrystals

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## Experimental Section

## I. Chemicals

Copper (Ⅱ) acetate (Cu(OAc), 99.99 %), zinc acetate (Zn(OAc), 99.99 %), tin (Ⅳ) chloride ($SnCl_2$, 99.99 %), thioacetamide (TAA, 99.99 %), hydrazine hydrate (hydrazine, 99.99 %, tri-sodium citrate ($Na_3C_6H_5O_7$, $Na_3$-citrate), tetra-acetate disodium salt ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, $Na_2EDTA$) and ammonia ($HN_4OH$, 28-30 %) were purchased from Aldrich and used as received.

## II. Preparation of CZTS nanocrystals

The precursor solution was prepared using 40 mL of 0.2M Cu(OAc), 40 mL of 0.1M Zn(OAc) and 40 mL of 0.1M $SnCl_2$. Subsequently, 40 mL of a 0.2M TAA solution was added and complexing agents including hydrazine (4 mL of 0.01 M, $Na_3$-citrate (4 mL of 0.01 M, and $Na_2EDTA$ (4 mL of 0.01 M) were further added. The pH was adjusted to 7 by adding an ammonia ($NH_4OH$) solution with constant magnetic stirring for 10 minutes at room temperature. During this step, the color of the precursor solution changed from a transparent to a brown-green. The precursor solution was placed in an auto clave container and then heated for 24 hours at 200 $^oC$ in an oven. The reacted solution was then cooled to room temperature in air. The powder formed in the solution was separated from the precursor solution by centrifugation at 3000 rpm for 10 minutes. This process was repeated three times. Finally, the precursor powder was dried in a vacuum oven at 60 °C for 8 hours.

## III. Characterizations

The crystallographic information of the synthesized NCs was characterized by powder X-ray diffraction (PXRD, PANalytical, X'Pert-PRO, and Netherlands) operated at 45 kV and 40 mA. The bright-field (BF) transmission electron microscopy (TEM) images, their corresponding selected area electron diffraction

(SAED) patterns, and the high-resolution (HR) TEM images of the synthesized NCs were obtained using a JEOL-3010 at an operating voltage of 300 kV. Elemental mapping images and energy-dispersive X-ray spectra were acquired using energy-dispersive X-ray spectroscopy (EDS) with a Tecnai G2 F30 installed in a scanning transmission electron microscope (STEM) equipped with a high-angle annular dark-field (HAADF) unit. The optical absorption and band gap energy of the synthesized NCs were measured by UV-visible spectroscopy (Cary 100, Varian, Mulgrave, Australia) at room temperature.

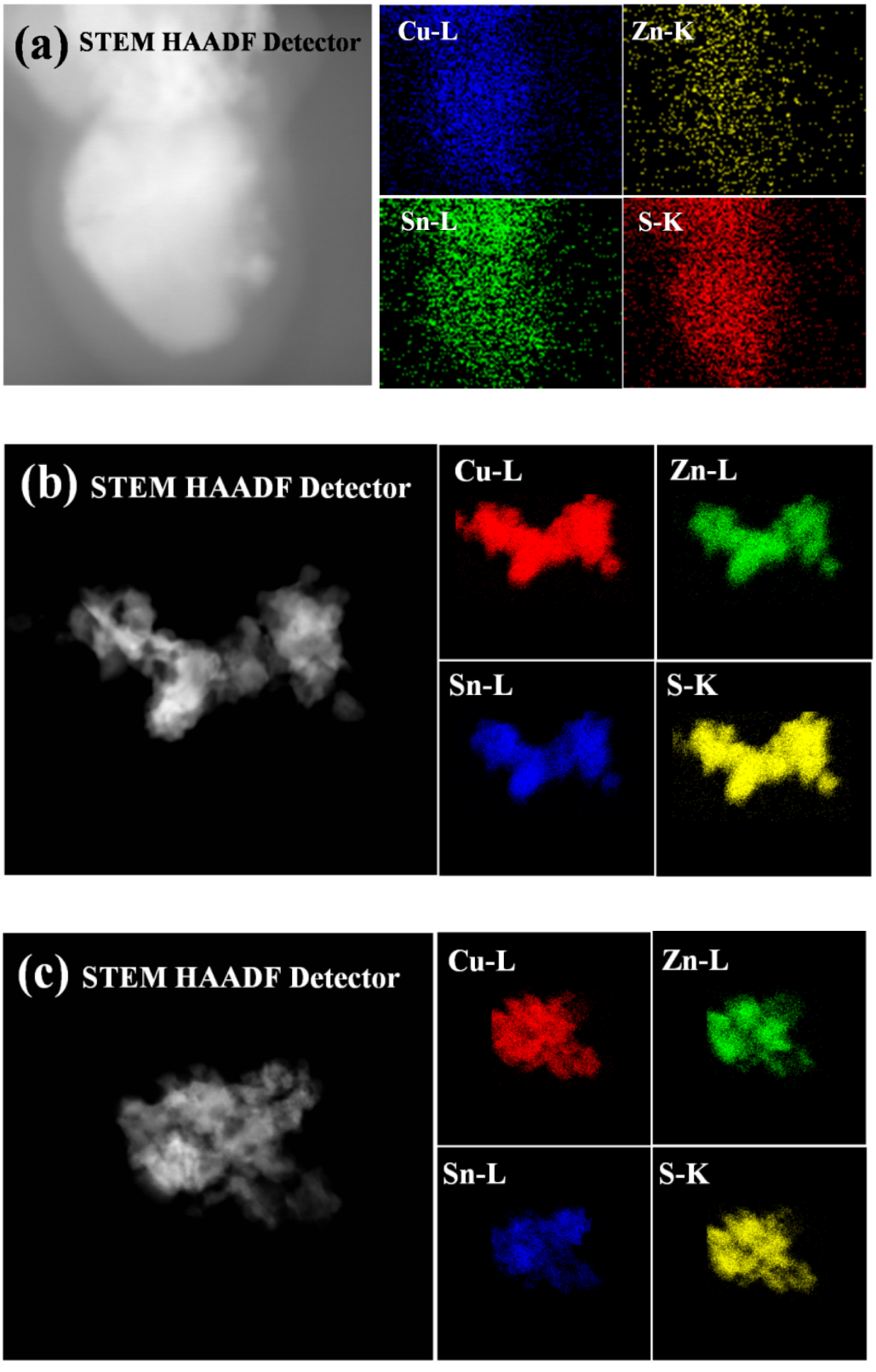


Figure S1. HAADF-STEM image and elemental mapping images of synthesized CZTS NCs prepared without complexing agent (a), with hydrazine (b), and with $Na_3$-

citrate (c). The images were obtained on carbon film-assisted Ni grids (200 mesh, Electron Microscopy Sciences) using a Tecnai G2 F30 equipped with a high-angle annular dark-field (HAADF) unit at an accelerating voltage of 300 kV.

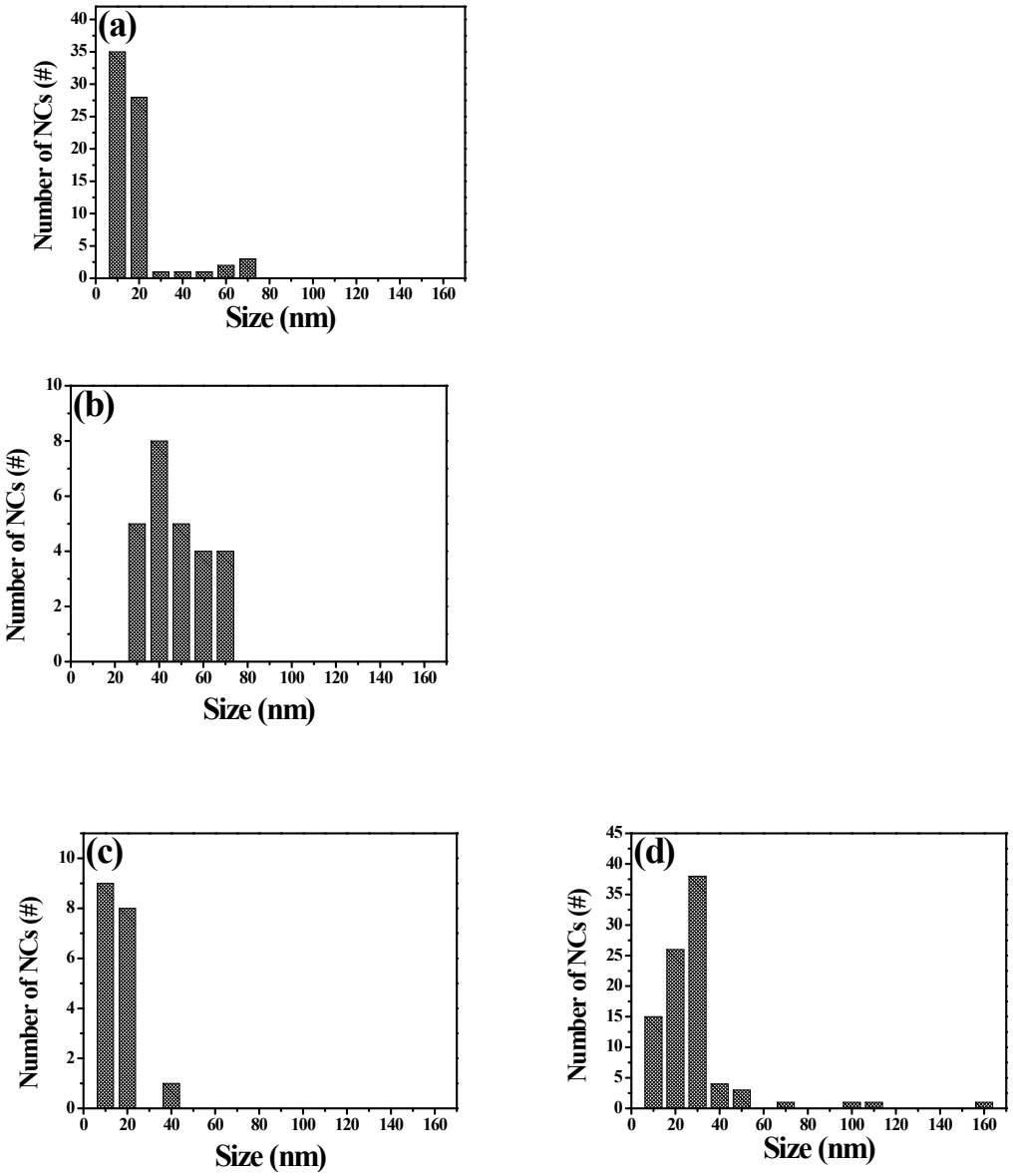


Figure S2. Size distribution of synthesized CZTS NCs prepared without complexing agent (a), with hydrazine (b), with $Na_3$-citrate (c), and with $Na_2EDTA$ (d).