## **Electronic Supplementary Information (ESI)**

## A top-down strategy to synthesize wurtzite Cu<sub>2</sub>ZnSnS<sub>4</sub>

## nanocrystals by green chemistry

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**Synthesis of Cu<sub>2</sub>O nanocubes.** In a typical synthesis, 1.5 mL of Cu(NO<sub>3</sub>)<sub>2</sub> ethanol solution (0.1 M) was dropwise added into 20 mL of NaOH aqueous solution (5.0 M) to form a deep blue solution ( $[Cu(OH)_4]^{2-}$  complexes) with magnetic stirring. Then, 200 mL of freshly-prepared ascorbic acid aqueous solution (0.015 M) was quickly added into the blue solution. The mixed solution was continuously stirred for 5 min at room temperature. The yellow product was collected and washed with distilled water several times.

## Synthesis of wurtzite CZTS nanoboxes and nanocrystals.

10 mL SnCl<sub>4</sub> aqueous solution (0.0375 M) was dropwise added into 20 mL Na<sub>2</sub>S solution (0.375 M) to form a transparent tin metal chalcogenide complex ( $[Sn_2S_6]^{4-}$ ) solution. Under magnetic stirring the as-prepared Cu<sub>2</sub>O nanocubes dispersed in 20 mL of distilled water followed with addition of 10 mL Zn(NO<sub>3</sub>)<sub>2</sub> aqueous solution (0.0375M). The pH value of the mixed suspension was adjusted to neutral (pH=7) by adding diluted HCl solution (0.03%). The suspension was transferred into a Teflon-lined stainless steel autoclave, which was then sealed and kept at 190 °C for designed durations, 4 h for the wurtzite CZTS nanoboxes and 24 h for the wurtzite CZTS nanocrystals. The black products were collected and washed with distilled water and absolute ethanol several times.

**Characterization.** The crystallographic structures of the various samples were characterized with X-ray diffraction (XRD, Rigaku D/Max 2500v diffractometer, Cu Kα radiation). Morphologies, sizes, crystal structures, and compositions were studied with scanning electron microscopy (SEM, Philips XL30 FEG), transmission electron

microscopy (TEM, Philips CM 200 FEG, 200 kV, or JEOL JEM-2100F, 200 kV), and energy-dispersive X-ray (EDX) spectroscopy. X-ray photoelectron spectroscopy (XPS) was performed in a Thermo ESCALAB 250Xi XPS spectrometer system with a monochromatic Al K $\alpha$  X-ray source (1486.6 eV). Raman spectra were measured with a Lab RAM HR Evolution system with a 532 nm excitation source. Absorption spectra were recorded with a Cary 5000 UV-Vis-NIR spectrophotometer. PL spectra were carried out with a Hitachi F-4600 fluorescence spectrophotometer with an excitation of 550 nm. Photoresponse properties were measured under AM 1.5G simulated sunlight at an intensity of 100 mW cm<sup>-2</sup>.



Fig. S1 XRD pattern of the  $Cu_2O$  nanocubes prepared by reacting  $[Cu(OH)_4]^{2-}$  complex solution with ascorbic acid.



Fig. S2 XRD pattern (a) and Raman spectrum (b) of the copper sulfide nanoboxes.



Fig. S3 SEM images of the wurtzite CZTS samples prepared for various durations: (a) 4 h, (b) 8 h, (c) 12 h, (d) 18 h, and (e) 24 h.



Fig. S4 Fast Fourier transform of the HRTEM image of wurtzite CZTS in Figure 3d, confirming the wurtzite hexagonal structure.



Fig. S5 EDX spectrum of the wurtzite CZTS nanocrystals prepared for 24 h.



Fig. S6 (a) XRD patterns of the samples obtained in growth solutions with various pH values after hydrothermal reaction of 24 h. (b) Raman spectrum, (c,d) SEM images, (e) TEM image, and (f) HRTEM image of the CZTS nanoboxes prepared in the growth solution at pH=12 for 24 h.



Fig. S7 XRD patterns (a) and Raman spectra (b) of the samples obtained in the growth solution at pH = 12 for various reaction time, indicating the evolution from  $Cu_{2-x}S$  nanoboxes to kesterite CZTS nanoboxes. It is also revealed that  $OH^-$  ions react with  $Sn^{4+}$  ions to form  $SnO_2$  in such a high pH solution.  $Cu_{2-x}S$  then reacts with  $SnO_2$  in the sulfide solution to produce kesterite CZTS. It well accounts for the formation of kesterite CZTS instead of wurtzite CZTS in the high pH solution.



Fig. S8 (a) XRD pattern of the CZTS nanocrystals after annealing at 300 °C, showing the transformation from the wurtzite phase to the kesterite phase. (b) UV-vis spectra of the as-prepared wurtzite CZTS nanocrystals and the kesterite CZTS sample obtained after annealing at 300 °C, exhibiting enhanced absorption properties after conversion from the wurtzite phase to the kesterite phase.