Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# Supporting Information

# Understanding the Phase Formation Kinetics of Nano-Crystalline Kesterite Deposited on Mesoscopic Scaffold *via* In-Situ Multi-Wavelength Raman Monitored Annealing

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## Experimental Section:

### Precursor preparation

$TiO_2$ mesoscopic film was prepared by doctor-blading of commercially available anatase paste (Dyesol, 18NR-T) on cleaned FTO glass, then slowly heated up to 450℃ and kept for 30 min to form the porous mesoscopic film. After, there are three steps for the quaternary precursor to be in-situ deposited and coated onto the mesoscopic $TiO_2$ film: 1. 100 mL 0.02M $SnCl_2$ and 0.16M $Na_2S$ aqueous solution were prepared separately in two containers. Then the as-prepared $TiO_2$ film on FTO glass was immersed into aqueous cationic solution containing $Sn^{2+}$ and aqueous anionic solution containing excess $S^{2-}$ successively with one-minute interval time; the process was repeated for 10 times to form a $SnS_x$ coating on the walls of the $TiO_2$ mesopores. 2. Similarly, ZnS was in-situ deposited with another 15 SILAR rounds, instead of $SnCl_2$, 100mL 0.1M $ZnCl_2$ aqueous solution was used as the cationic source. 3. To complete the precursor preparation, copper was incorporated by an additional ion-exchange step. Briefly, 100mL 0.02M copper(II) chloride aqueous solution (pH~4) was prepared, then the ternary sulfide (Sn-Zn-S) coated $TiO_2$ film was immersed into the Cu solution and kept for 9 minutes. At the end of this immersion stage, the color of the film changed from red-brown to black indicating that ion-exchange had led to CZTS precursor coated onto $TiO_2$ mesoporous film. Finally, the films were washed with deionized water before subjected to characterization and annealing. More details are provided in a previous publication (ref. 23, Crystal Growth & Design, 2016, 16, 3618–3630).

**In-situ Raman annealing/characterizations**

Raman spectroscopy was performed using a Renishaw inVia Raman spectrometer equipped with a LEICA optical microscope. Available excitation light sources are four lasers with wavelength of 488 nm, 514 nm, 633 nm and 785 nm with measured power of 0.5 mW, 0.5 mW, 0.2 mW and 0.1 mW, respectively (the power indicated were measured on the laser illumination out of the 5X object lens of the optical microscope by power meter); Transmission Electron Microscope (FEI Tecnai G2 F20 200 kV Cryo-STEM equipped with EDAX Genesis EDS) is used to investigate the size and shape of CZTS nanocrystals coated on $TiO_2$ as well as the uniformity of distribution at nanoscale.

In-situ annealing was performed with a cold/hot stage (Linkam) mounted under the LEICA microscope. The glass window of the stage allows the transmission of optical signals. Heating and cooling rate was controlled at 30 K/min and constant $N_2$ flow is kept to provide an inert atmosphere inside the sample chamber for the whole time. When starting the heating program, hot plate temperature under sample is precisely controlled and Raman spectrum is captured at the mean time. It is clarified here that when a holding time at a certain annealing temperature is given for a sample, say 1min, it should be understood that the sample has already gone through the heat-up period at the fixed rate of 30℃/min. The laser power applied has been optimized on one hand to obtain better revolved kesterite Raman peaks, on the other hand to avoid the issue of illumination damage/peak broadening. Meanwhile, to reduce the light exposing time (accumulated heat from illumination), we set the program to close the light shutter once spectrum capturing is finished. By these means we ensure that the light induced damage is minimized during the in-situ Raman measurements. However, the other issues like the in-situ Raman spectrum acquisition delay during the annealing could induce errors for analysis of phase formation kinetics. Improvement to this regard is underway as future work.

## Data processing for Raman spectra

The normalized intensity was presented to better study the Raman profile change for a sample during in-situ Raman. It was calculated by defining the highest peak intensity of kesterite or copper sulfide as 1 and plotting the ratio of the rest. FWHM and peak center position were extracted by fitting the spectra with symmetrical Lorentz peaks using the residuals method; instead of using two peaks to fit the main kesterite mode, we used only one peak to best describe the main mode. Detailed fitting results are shown in Figure S4.

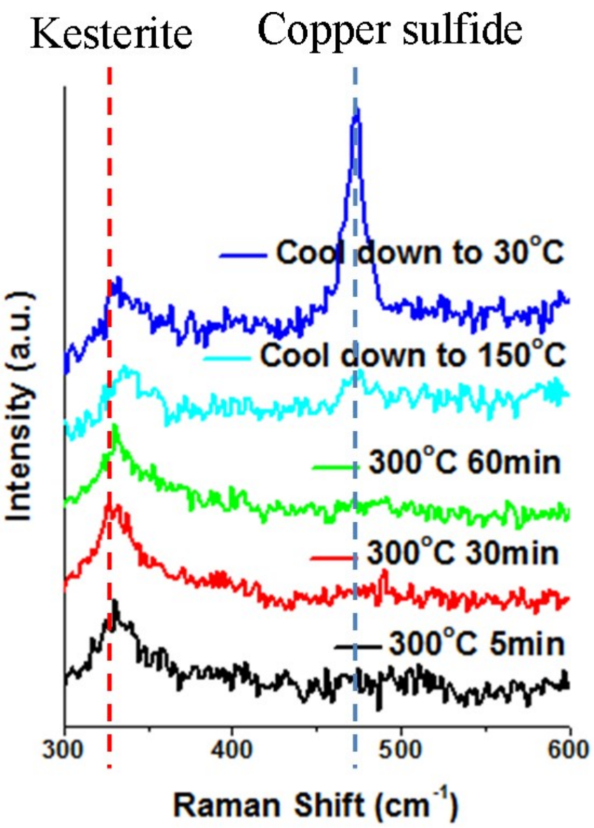

Figure S1. In-situ Raman monitored annealing with 514 nm laser at 300℃for 60min followed by cooling down.

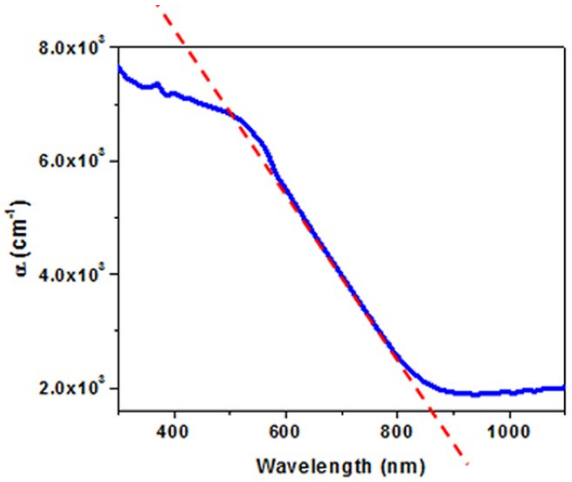

Figure S2. Light absorbance spectrum of a CZTS-coated $TiO_2$ mesoporous film.

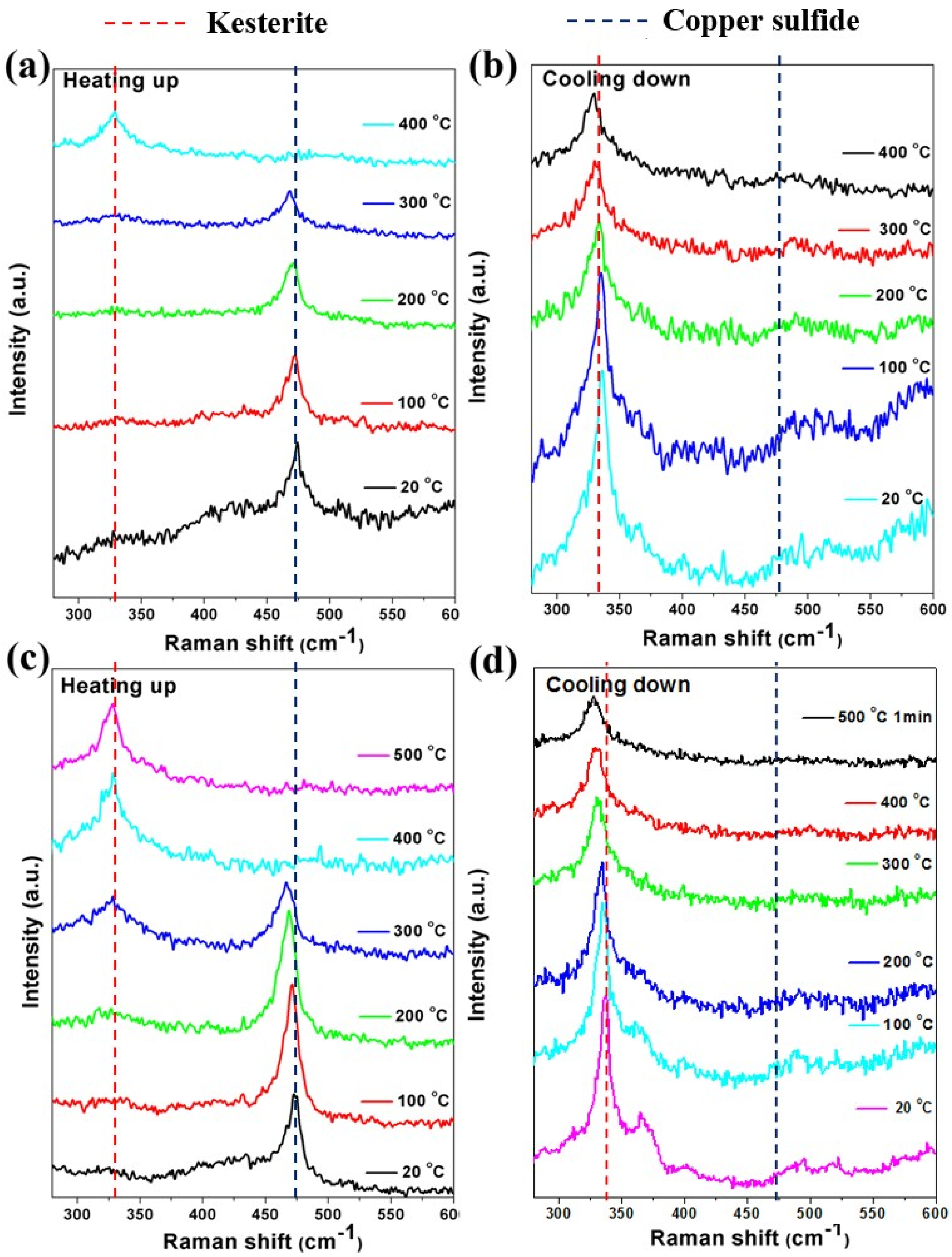

Figure S3. In-situ Raman monitored annealing at a), b) 400℃ and 1min; and c), d) 500℃ and 1min with 633 nm laser. Spectra were taken every minute for a total of 19 minutes.

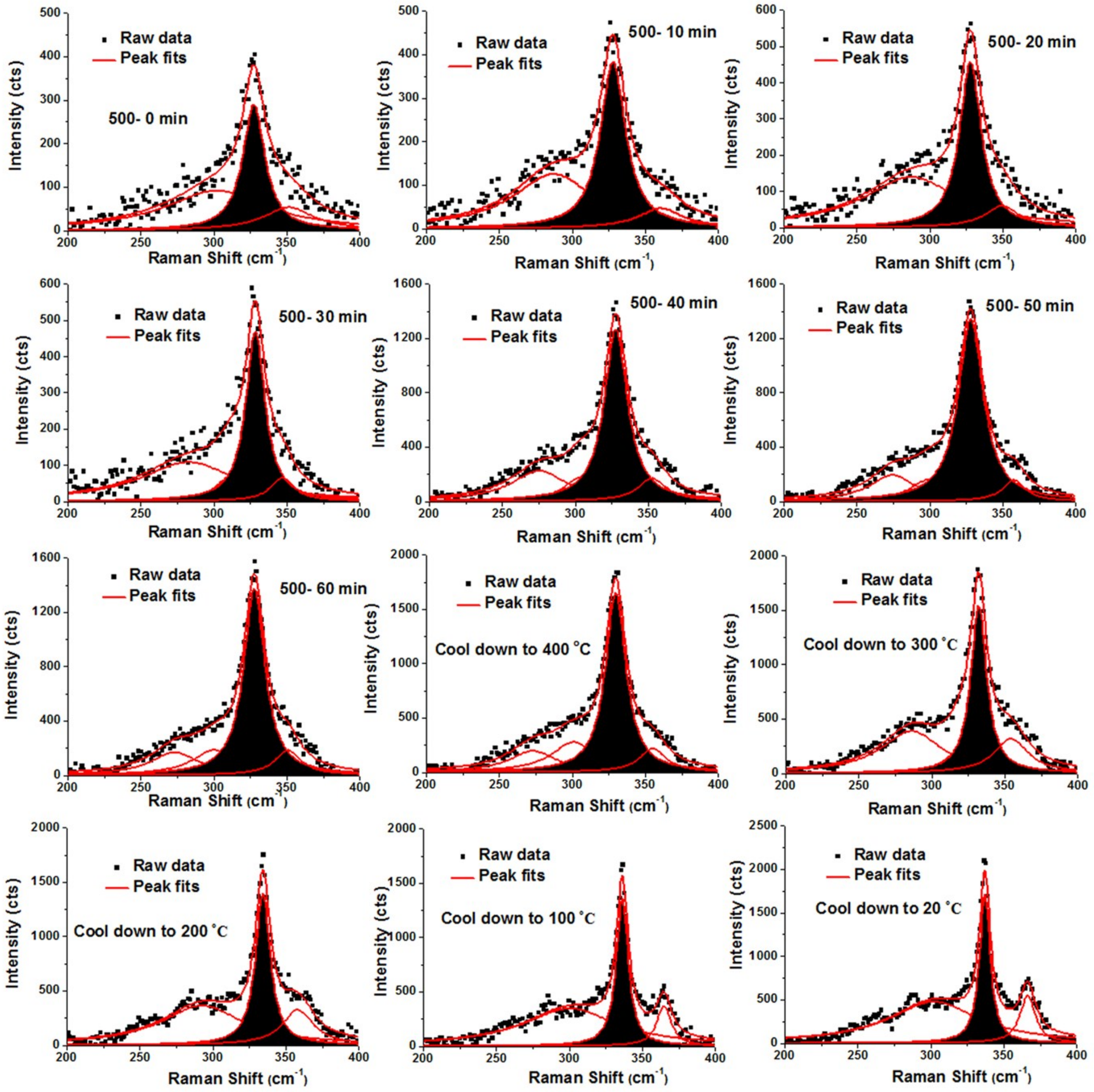

Figure S4 Lorentzian peak fits of the 500℃, 1h in-situ Raman spectra; the peaks filled with black represent the main kesterite mode.