Mesofluidic Synthesis of Cu2ZnSnS4 Nanoparticles for Solar Cell Applications

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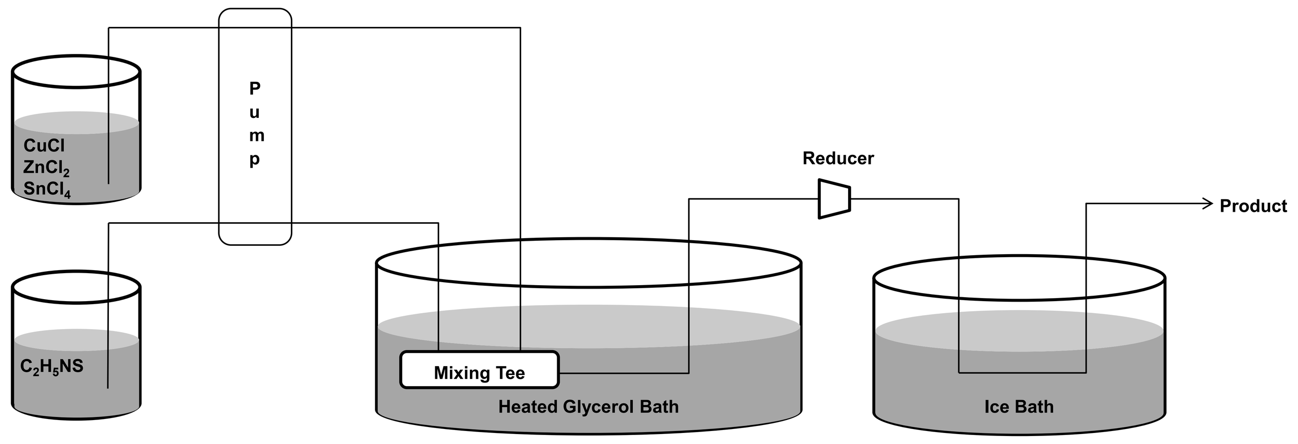
Overview

- Cu_2ZnSnS_4 (CZTS) is a promising absorber for low cost thin film solar cells due to its excellent optical properties and relatively high abundance of its constituent elements.
- CZTS is isoelectronic with $CuIn_xGa_{1-x}Se_2$ (CIGS), a close structural analog that is currently used in commercial thin film solar modules. The relatively high prices of indium and gallium may impact the levelized cost of electricity for CIGS modules, where indium and gallium are roughly 300 times the price of zinc and 25 times the price tin, which is one of the main drivers for considering CZTS as a replacement material.
- In this work CZTS nanoparticles were continually synthesized in a mesofluidic flow reactor. The flow was segmented in a controlled manner by gas generation within the reactor to assist in narrowing the particle size distribution. The composition of the nanoparticles was controlled by optimizing the residence time, reaction temperature, and concentration of precursors.

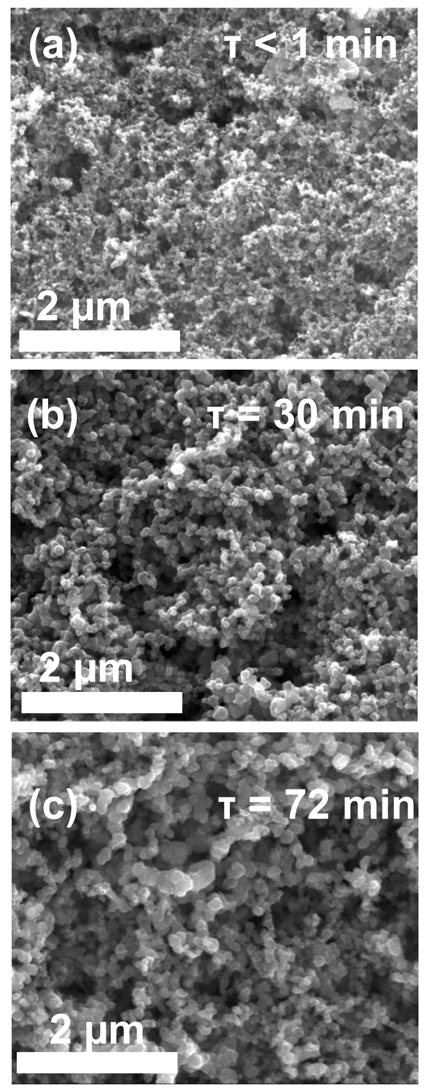
Reactor setup



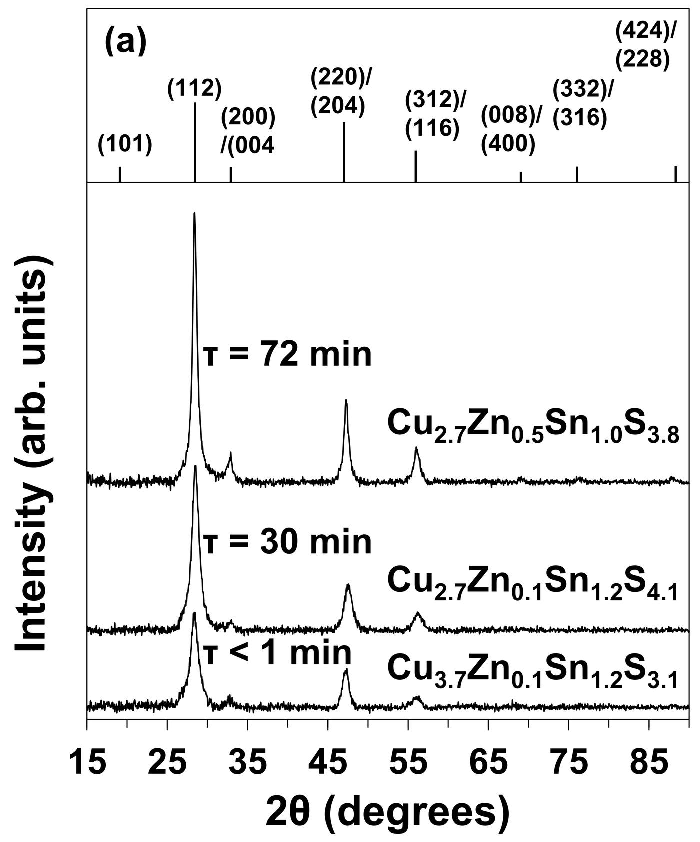
Effect of Residence Time on Nanoparticle Size, Structure, and Composition

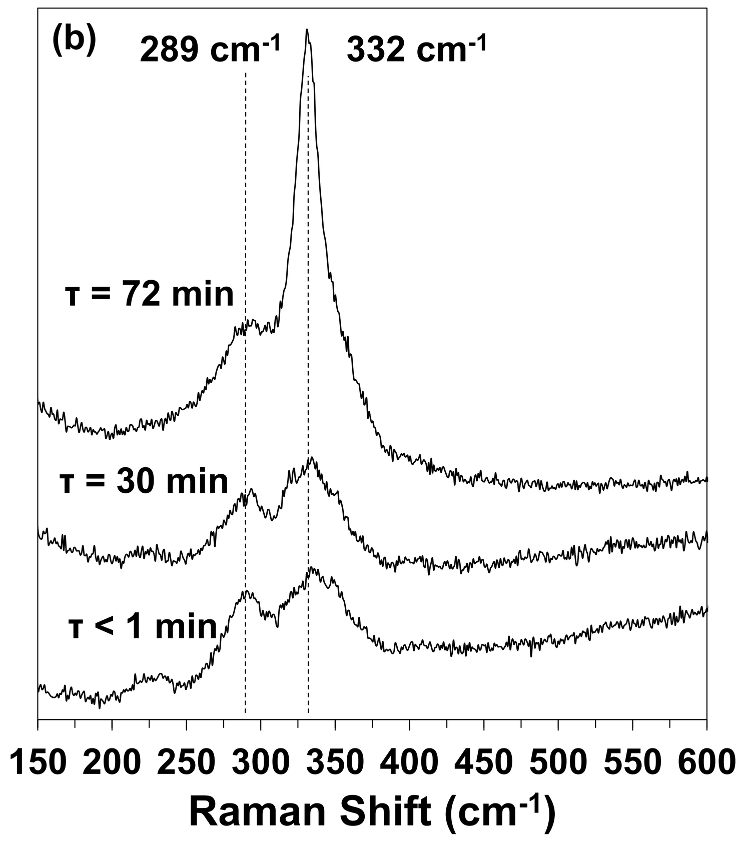
Residence time, min	Composition, atomic %				Crystallite size,# nm
	Cu	Zn	Sn	S	
< 1	44.15	1.36	15.37	39.13	7.6
30	33.19	0.88	14.52	51.44	8.6
72	33.77	6.27	12.12	47.85	13.8

CZTS precursor solutions reacted at 215 ^{0}C.
As residence time increases, copper concentration decreases while zinc concentration increases.
#Crystallite size increases for longer residence times, as determined by XRD.



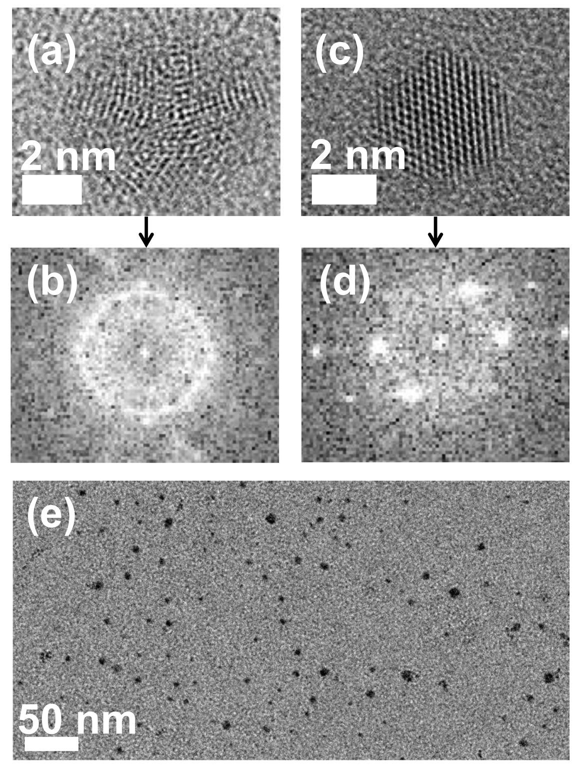
50,000x magnification SEM images of nanoparticles reacted for (a) < 1 min, (b) 30 min, and (c) 72 min.



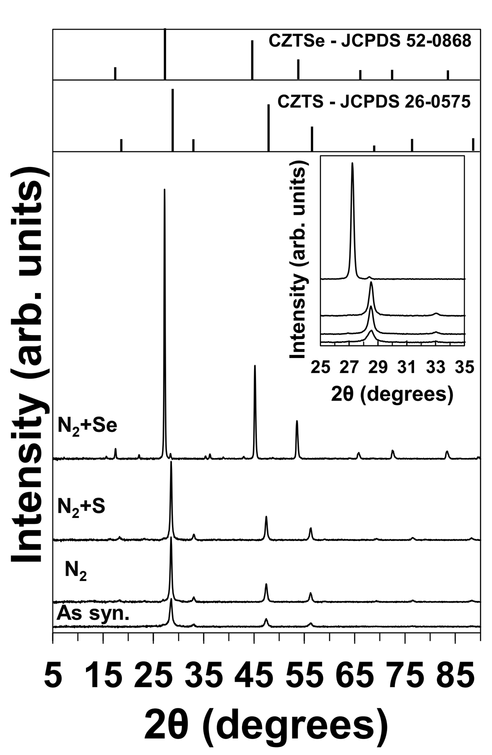


(a) XRD and (b) Raman spectra for CZTS nanoparticles synthesized for different residence times. The composition, as determined by EDS, is also shown for the corresponding residence time.

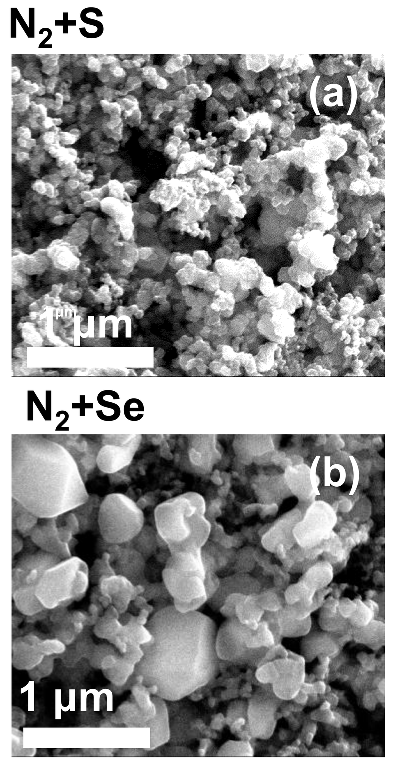
Optimization of Nanoparticle Composition and Annealing Studies



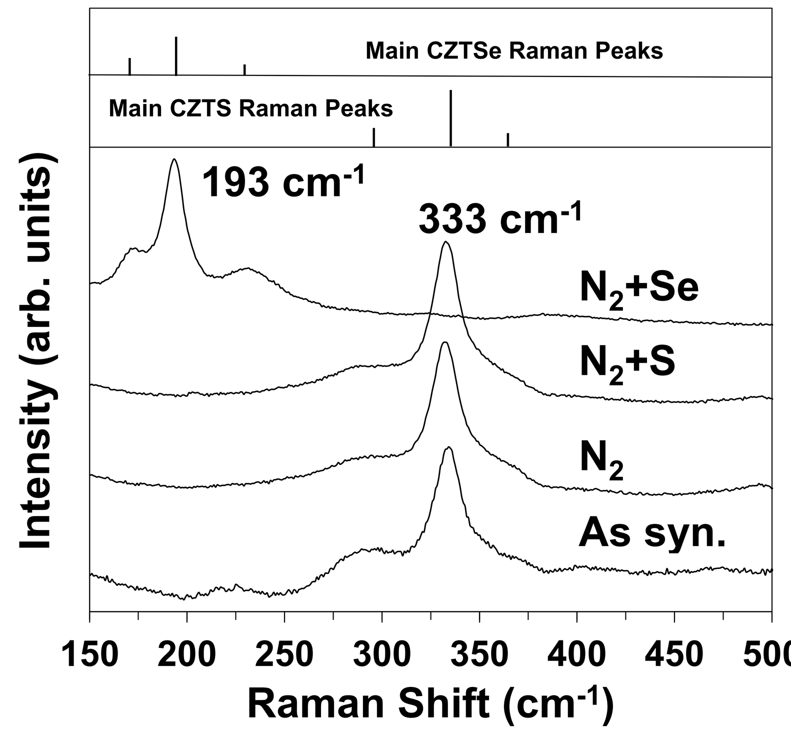
After optimizing the CZTS composition, TEM analysis shows that the as synthesized CZTS nanoparticles are both (c,d) single and (a,b) multicrystalline with an (e) average size of 5.4 nm.



XRD spectra of CZTS nanoparticles after annealing in N_2, N_2+S, and N_2+Se. Selenium substitution is indicated by the shift to lower angles.



CZTS nanoparticles annealed in (a) N2+S and (b) N2+Se environments. Larger grain growth was observed when annealing in the N2+Se atmosphere.



Raman spectra from annealed CZTS films. Main vibrational modes of CZTS shift after selenization, indicating conversion to selenide.

Conclusion

- Demonstrated self-segmented, continuous flow production of CZTS nanoparticles
- Nanoparticle composition varies with residence time
- CZTS converted to CZTSe via selenization at 500 ^{0}C.

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