

Supporting Information

Facile Synthesis of Single Crystalline Sub-micron $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) Powders using Solvothermal Treatment

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Experimental

Fabrication of dye-sensitized solar cells (DSSCs)

The preparation of TiO_2 photoelectrodes were prepared from standard doctor blade technique using commercial TiO_2 paste (Dyesol 18NRT, Dyesol) followed by annealing and dye loading (ethanolic 0.5 mM N719 dye solution (Dyesol)). The CZTS/FTO counter electrode (CE) was prepared by spin-coating. In a typical process, the as-prepared CZTS powder were dispersed in 10 mL of ethyl alcohol and under ultra-sonication for 1 h to form a uniform 'ink' of CZTS. The 'ink' was then spin-coated onto a clean fluorine-doped tin oxide (FTO) glass substrate with a exposed area of $10 \times 15 \text{ mm}^2$. The films were completely dried and then annealed at $100 \text{ }^\circ\text{C}$ in air. For comparison, Pt-coated FTO was used as a CE (purchased from Dyesol). DSSCs with an active area of 0.25 cm^2 were fabricated with a photoanode (a TiO_2 film sensitized by N719, Dyesol, Australia), a CE and an electrolyte containing 0.06 M LiI, 0.6 M 1-butyl-3-methylimidazoliumiodide, 0.03 M I_2 , 0.5 M 4-tert-butyl pyridine and 0.1 M guanidinium thiocyanate in acetonitrile.

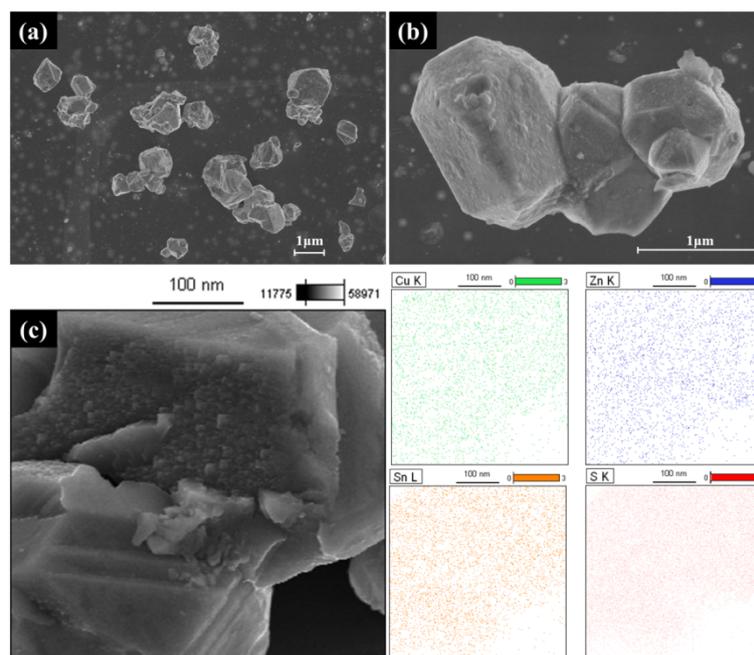
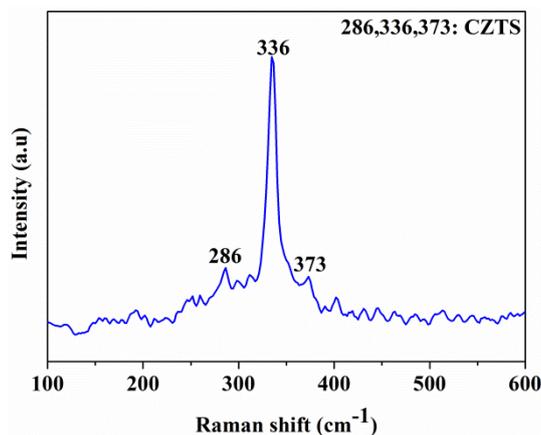


Figure S1 SEM images (a) (b) and EDS elemental map of CZTS particles (c) synthesized at $400 \text{ }^\circ\text{C}$ for 5h.

Table S1 Elemental ratios of the CZTS powders prepared at 400 °C for 5 h.

Sample	EDS estimated composition ^a	[Zn]/[Sn]	[Cu]/[Zn+Sn]
	(% atomic ratio Cu/Zn/Sn/S)	~1.25(Expected)	~0.9(Expected)
CZTS-5	23.27/12.59/13.58/50.5	0.93	0.88

**Figure S2** Raman spectra for the CZTS powders formed at 400 °C for 5 h, with the 325 nm He-Ne laser as the excitation source.**Table S2** Comparison with the lattice parameters of CZTS using various synthesis methods.

Method	Size distribution /nm	a (5.427 standard)/Å	b (5.427 standard)/	c (10.848 standard)/	Ref.
Solvothermal (400 °C,5h)	500-1000	5.430	5.430	10.828	Present work
Solvothermal (230 °C,24h)	~25	5.396	5.396	10.834	1
Microwave hydrothermal method (700W,10min)	10-100	5.420	5.420	10.848	2
Solvothermal (190 °C,24h)	~50	5.428	5.428	10.762	3
Solvothermal (180 °C,24h)	~5	5.400	5.400	10.800	4
Electrospinning with post annealing	100-150	5.440	5.440	10.890	5
Solvothermal (200 °C,16h)	150-300	5.431	5.431	10.826	6

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