Electronic Supplementary Information for:

Optimization of Cu_2ZnSnS_4 Nanocrystal Recipe by means of Photoelectrochemical Measurements

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1. Instrumentation

The PEC set-up consisted of a 150 W Newport lamp with an AM 1.5D filter, and a CH Instruments potentiostat. The NC film on the ITO-PET plate was the working electrode submerged in a 0.1 M $MVCl_2$ electrolyte solution. A platinum and standard calomel electrode (SCE) were used as counter and reference electrodes. Current was measured versus applied potential sweeping from 0 to -0.400 V while chopped light was directed onto a 10.0 mm^2 area of NC film at a frequency of 0.17 Hz.

Scanning electron microscopy (SEM) was performed on a Hitachi S-4500 field emission microscope with an EDS system. Transmission electron microscopy (TEM) was done on a Philips CM 10. Powder X-ray diffraction (XRD) was examined on an Inel CPS Powder Diffractometer with Cu X-ray radiation source. X-ray photoelectron spectroscopy (XPS) was investigated on a Kratos AXIS Nova Spectrometer with an Al Kα X-ray source.

2. Absorption Spectroscopy

An absorbance spectrum taken for CZTS prepared via one-pot method dispersed in acetone solution. The squared values of the absorbance were plotted versus the energy of the light in order to give a rough determination of the bandgap of the material.[S1]

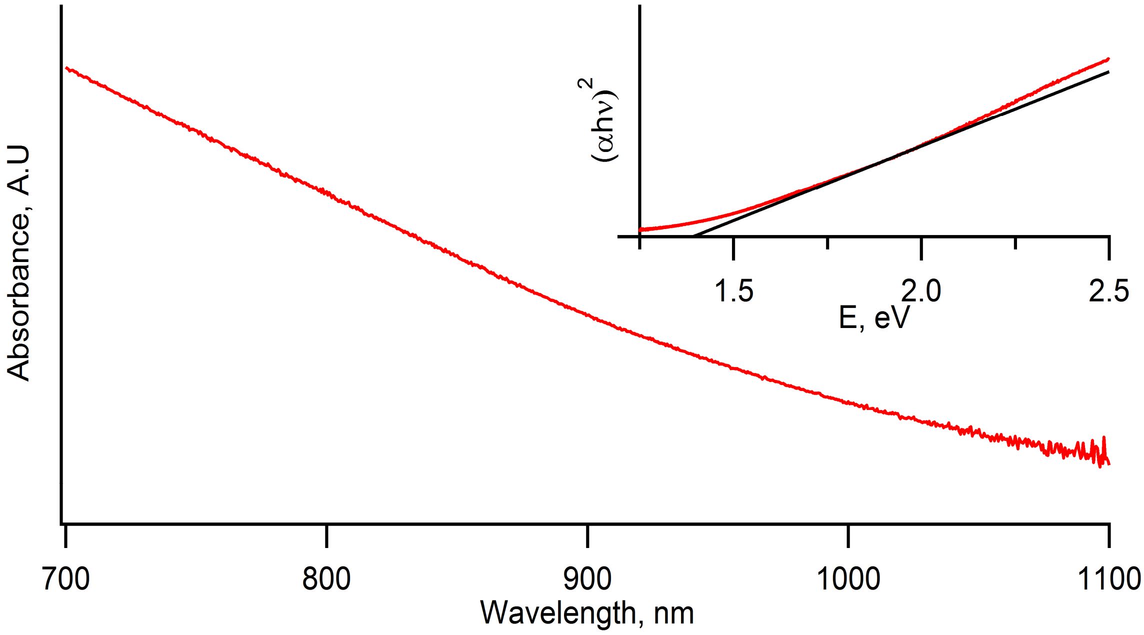

Fig. S1. Absorbance measurement of as-synthesised CZTS nanoparticles, the inset shows an obtained band gap of 1.4 eV.

3. Action Spectra

The description of the photoactivity of the CZTS samples on ITO-PET at specific wavelengths at varying applied potentials. This photoactivity indicates the peak wavelength for which the CZTS samples absorb and generate electrons most effectively and also allows for information on the bandgap to be collected. The peak photocurrent will determine which energy of light corresponds to the bandgap of the CZTS nanocrystals. It was determined through these spectra that the bandgap of the CZTS was approximately 1.40eV, which corroborated the data obtained by the absorption spectrum.

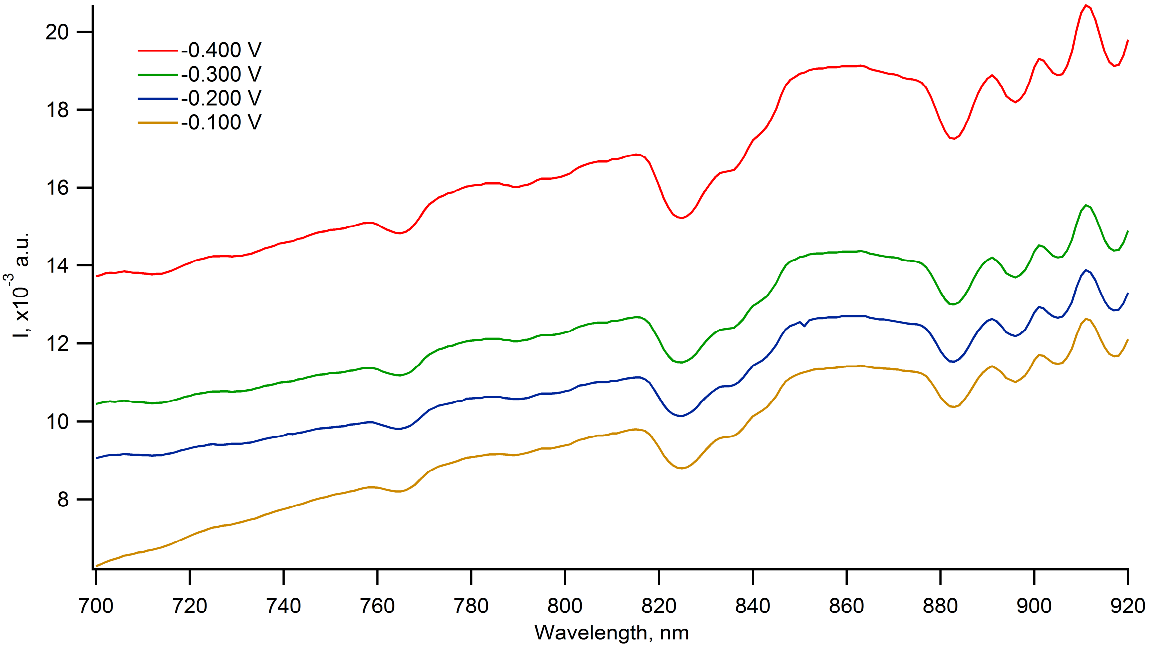

Fig. S2. Action spectrum of CZTS electrode for different applied potentials.

4. Supplementary XPS Spectra

Expanded XPS spectra that highlight secondary peaks for Cu, Zn and Sn for the two types of electrodes presented within the paper: the working D70 and the non-working A50. The Zn spectra for A50 could not be reolved further due to the obstruction of the $2p_{1/2}$ peak by the Sn MNN Auger peak.

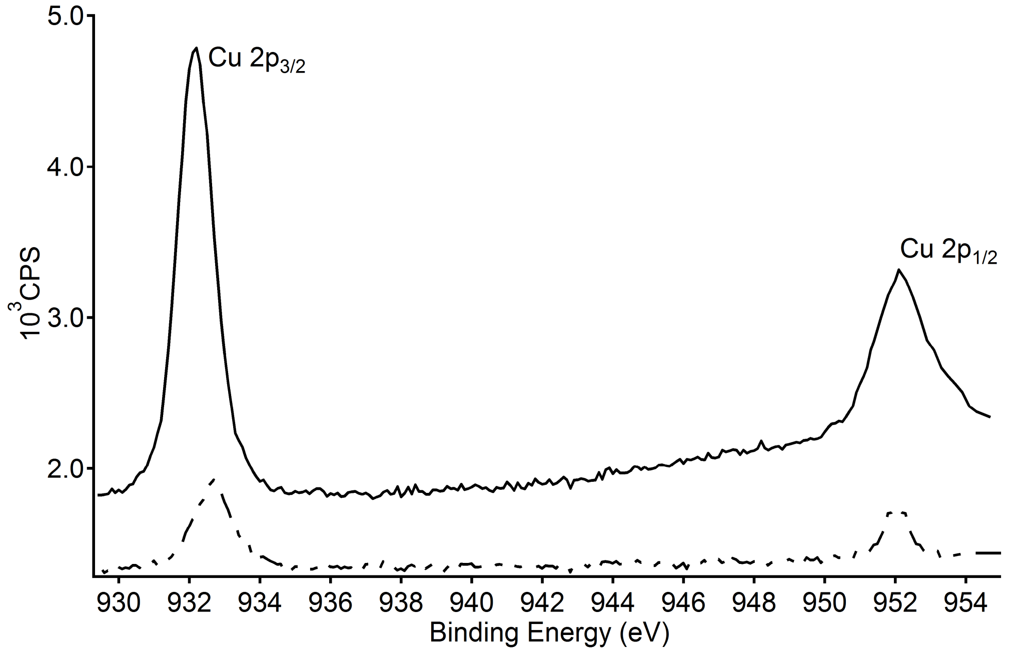

Fig. S3. Cu 2p XPS spectra for D70 (solid lines) and A50 (broken lines).

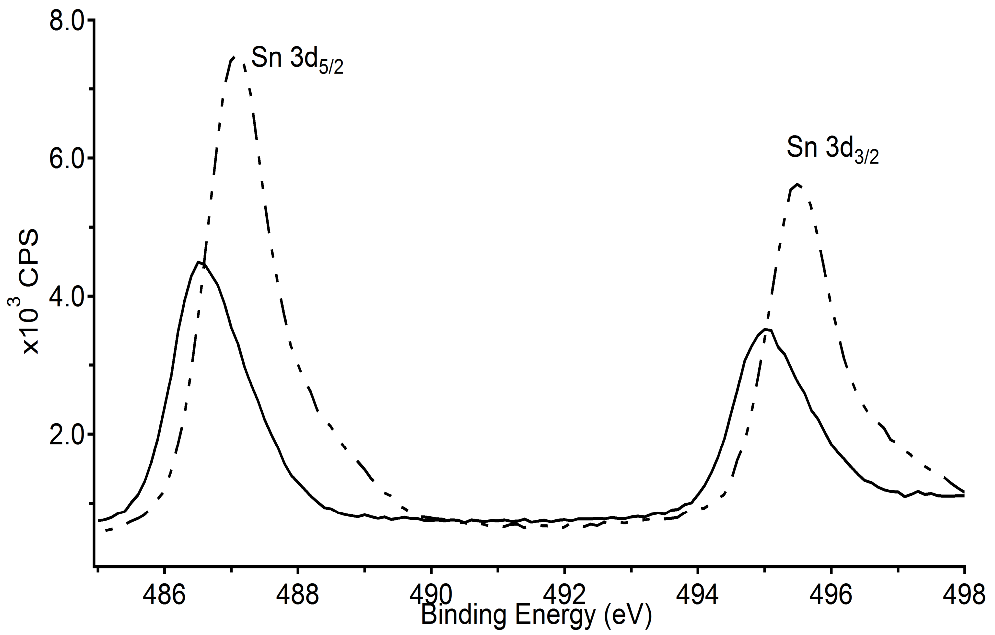

Fig. S4. Sn 3d XPS spectra for D70 (solid lines) and A50 (broken lines).

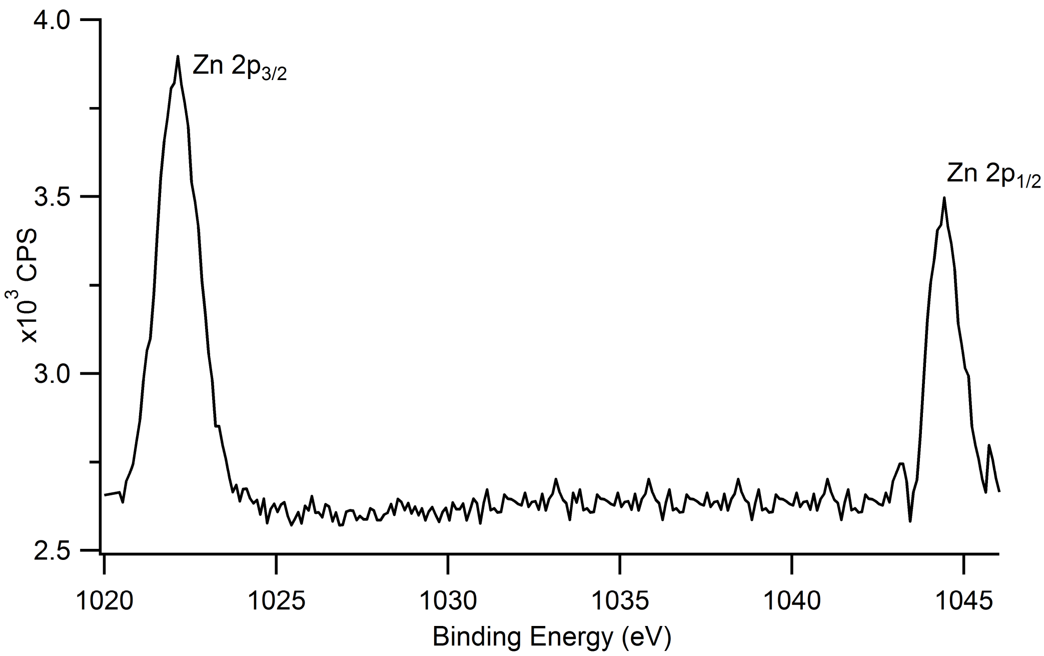

Fig. S5. Zn 2p XPS spectra for D70.

References

S1. M. Cao and Y. Shen, *J. Crystal Growth*, 2011, **318**, 1117-1120.