



Solution-processed Cd-substituted CZTS nanocrystals for sensitized liquid junction solar cells



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ABSTRACT

The Earth-abundant kesterite Cu₂ZnSnS₄ (CZTS) exhibits outstanding structural, optical, and electronic properties for a wide range of optoelectronic applications. However, the efficiency of CZTS thin-film solar cells is limited due to a range of factors, including electronic disorder, secondary phases, and the presence of anti-site defects, which is a key factor limiting the V_{oc} . The complete substitution of Zn lattice sites in CZTS nanocrystals (NCs) with Cd atoms offers a promising approach to overcome several of these intrinsic limitations. Herein, we investigate the effects of substituting Cd²⁺ into Zn²⁺ lattice sites in CZTS NCs through a facile solution-based method. The structural, morphological, optoelectronic, and power conversion efficiencies (PCEs) of the NCs synthesized have been systematically characterized using various experimental techniques, and the results are corroborated by first-principles density functional theory (DFT) calculations. The successful substitution of Zn by Cd is demonstrated to induce a structural transformation from the kesterite phase to the stannite phase, which results in the bandgap reduction from 1.51 eV (kesterite) to 1.1 eV (stannite), which is closer to the optimum bandgap value for outdoor photovoltaic applications. Furthermore, the PCE of the novel Cd-substituted liquid junction solar cell underwent a four-fold increase, reaching 1.1%. These results highlight the importance of substitutional doping strategies in optimizing existing CZTS-based materials to achieve improved device characteristics.

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1. Introduction

Solar energy technologies are considered to be one of the most promising alternatives to fossil fuels to meet the rising demand of clean and renewable energy [1–3]. The sun provides more than enough power to the Earth each second, which if harnessed correctly could satisfy the entire annual human energy demand after only a couple of hours. However, significant improvements in the rational

design of Earth-abundant absorber materials are still necessary before solar energy technology becomes more widely available [4–6]. Several research activities over the last decades have shown that the choice of suitable absorber materials coupled with efficient charge transport layers at the electrode-electrolyte interface are extremely important to achieve improved power conversion efficiencies (PCEs) [7–9]. Due to this, liquid junction solar cells (LJSCs) have received increased attention for next-generation photovoltaics [10]. In particular, LJSCs are more favourable than conventional dye-sensitized solar cells (DSSCs) owing to their low fabrication cost [11,12].

In general, LJSCs are composed of a semiconductor electrode and a counter electrode immersed in a suitable redox electrolyte [13]. In the past decade, binary semiconductor quantum dot materials, such

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as CdS, CdSe, CdTe, PbS or PbSe, have been employed as a sensitizer for quantum dot dye-sensitized solar cells (QDSSCs) [14]. However, most QDSSCs show a low power conversion efficiency (PCE) of up to 8% due to their restricted light harvesting range [15]. Hence, to broaden the light absorption range, the binary sensitizer has been replaced by quaternary chalcopyrites, such as CuInSe₂ (CIGSe) or Zn-Cu-In-Se (ZCISE), which have achieved PCEs of 11.49% and 12.57%, respectively, as liquid junction QDSSCs [16,17]. There are some limitations to the commercialization of CIGSe and ZCISE solar cells such as compositional uniformity, process control, toxicity and difficulties in large-scale industrial manufacturing [18].

Cu₂ZnSnS₄ (CZTS) has emerged as a promising alternative absorber candidate due to its composition of environmentally friendly and Earth-abundant elements, good absorption coefficient (10⁴ cm⁻¹) and direct optical band gap (1.0–1.5 eV) [19]. Owing to these outstanding properties, Bai et al. achieved a PCE of 3.29% for CZTS QDSSCs by the hydrolysis approach and a PCE of 4.70% for CZTS/CdSe QDSSCs [20]. Further to this, Xu et al. used CZTS microsphere-coated FTO as a counter electrode and achieved a power conversion efficiency of 3.73% [21]. However, it has been reported that the PCE of CZTS sensitized solar cells are still lower than other types of sensitizers due to insufficient light absorption, the presence of secondary phases, and short minority-carrier lifetimes [11]. Moreover, another major factor limiting the performance of kesterite CZTS is the formation of antisites (Cu_{zn}), which occurs due to the similar sizes of Cu and Zn ions [22].

A recent study has shown that cation substitution by heavier atoms like Cd may inhibit the formation of antisite defects, thereby increasing the minority carrier lifetime and reducing electronic disorder in the system [22]. There are multiple benefits of Cd-substitution in CZTS. Due to a relatively large negative enthalpy of formation of ZnS, a narrow single-phase region and accompanying undesired secondary phases are formed in CZTS structures [23]. Cadmium sulfide (CdS), with a less negative enthalpy, can reduce secondary phases; therefore favouring the single-phase region of CCTS [23]. Recently, Rondiya et al. have employed a combined experimental and theoretical approach to determine the band alignment and offset at CCTS/CdS and CZTS/CdS hetero-interfaces, observing a smaller conduction band offset at the CCTS/CdS interface [24]. It has been reported that the effective minority carrier lifetimes of CZTS and CCTS were calculated to be 10.8 and 4.1 ns, respectively, indicating that Cd incorporation improves the lifetime of the CZTS absorber, which is crucial to achieve enhanced photocurrent [25]. Further, Yan et al. elaborated in detail how Cd alloying can improve the current density of CZTS [26]. This review indicates that the introduction of Cd exerts a beneficial impact on the efficiency of CZTS solar cells. However, to the best of our knowledge, there is no report available on the solution-processed Cd-substituted CZTS absorbers for nanocrystalline sensitized liquid junction solar cells.

In the present work, we have synthesized CCTS and CZTS NCs through a cost-effective, low-temperature, and robust hot injection method. The crystal structure, size distribution, and surface morphology of the NCs are characterized using X-ray diffraction (XRD), Raman spectroscopy, (high-resolution) transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), and complementary density functional theory (DFT) calculations. The CZTS and CCTS devices were prepared by sandwiching the photoanode (FTO/TiO₂/CdS/CZTS(CCTS)/ZnS) and counter electrode (CuS/FTO) using 50 μL electrolyte solution (S⁻/S_n⁻). We have used ZnS as a passivating layer to overcome charge carrier recombination. As a result, we observed an improvement in the current density (J_{sc}) and open circuit voltage (V_{oc}) parameters of the CCTS NCs sensitized solar cell compared to the CZTS counterpart. We have achieved 1.1% efficiency for CCTS NCs sensitized solar cell compared to 0.25% for CZTS, and to the best of our knowledge, this is the first report of PCE > 1% for CCTS NCs sensitized solar cells. We also anticipate that

the efficiency of the CCTS NCs can be increased further through optimization of each layer in the device architecture.

2. Experimental and computational details

2.1. Chemicals

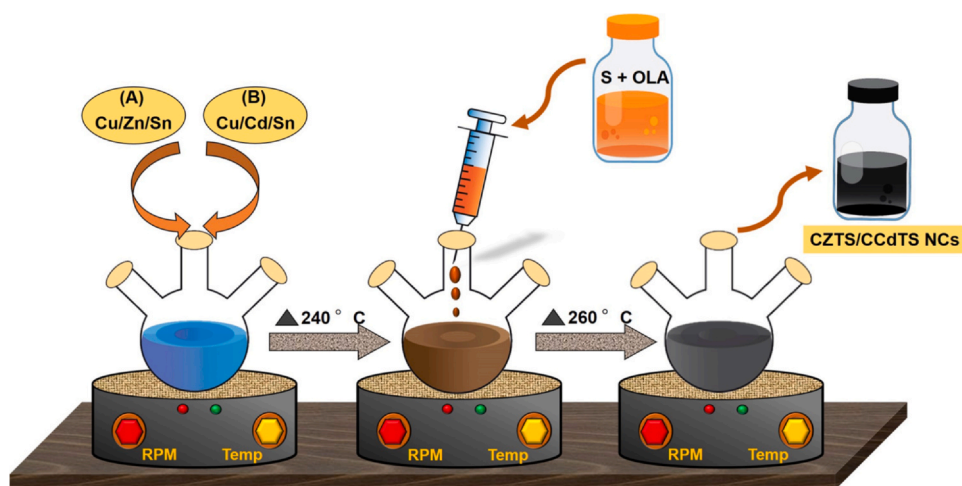
copper (II) acetylacetonate (Cu(C₅H₇O₂)₂, ≥ 97%), cadmium acetylacetonate (Cd(C₅H₇O₂)₂, ≥99.9%), zinc acetylacetonate Zn(C₅H₇O₂)₂, ≥ 99.99%), tin (IV) bis (acetylacetonate) dibromide ([CH₃COCH=C(O-)CH₃]₂SnBr₂, ≥ 97%), oleylamine (OAm, ≥ 99%), isopropanol (IPA, ≥ 99.5%), toluene (≥ 99.8%), were all purchased from Sigma-Aldrich and used as-received.

2.2. Synthesis

The colloidal synthesis of CZTS and CCTS NCs was carried out using the hot injection method as per our previous reports [24,27,28]. In a typical synthesis of the CZTS NCs, copper (II) acetylacetonate (1.5 mmol), zinc acetylacetonate (0.75 mmol) and tin (IV) bis (acetylacetonate) dibromide (0.75 mmol) were dissolved in 15 mL oleylamine in a 100 mL three necked flask under inert atmosphere. The solution was initially heated to ~135 °C under vacuum and degassed for 1 h and then maintained in nitrogen (N₂) until completely soluble. This procedure was followed by an increase in temperature to 240 °C, which leads to the formation of a metal oleylamine complex yielding a clear brown transparent solution. A freshly prepared sulfur precursor solution, 1 M sulfur powder dissolved in 3 mL oleylamine, was swiftly injected into the metal oleylamine complex solution which changed the solution color from transparent brown to a dark black. The flask temperature was maintained at 260 °C for 60 min to allow the growth of NCs. The temperature of the flask was then quickly brought down to ~80 °C by ice bath cooling. The reaction was further quenched by adding a solution of 5 mL of toluene and 40 mL of isopropanol. The colloidal solution from the flask was centrifuged at 10,000 rpm for 5 min, then the supernatant was decanted and the precipitate was obtained. The process was repeated for the whole solution from the flask. The final precipitate obtained was then dispersed in isopropanol and the solution was transferred to a petri dish for drying. The final solid product was dried under vacuum and stored in a vacuum desiccator. The synthesis of CCTS NCs was carried out by a similar method, but zinc acetylacetonate was replaced by cadmium acetylacetonate. The schematic of the facile hot injection setup and synthesis steps for the synthesis of CZTS and CCTS NCs is shown in Scheme 1.

2.3. Solar device fabrication

The fluorine-doped tin oxide (FTO) glass substrate was cleaned by isopropanol and distilled water followed by drying in an oven at 60 °C. The blocking layer was coated using TiCl₄ at 70 °C for 30 min. The first compact layer of TiO₂ (20 nm) and the second scattering layer of TiO₂ (~250 nm) were coated onto the FTO substrate using the doctor blade method [29]. After each layer of coating, the films were annealed at 450 °C for 1 h. Over the FTO/TiO₂ layer, we have deposited CdS as the buffer layer using the SILAR method [30]. The light absorber materials CZTS and CCTS were then deposited by our unique room temperature method. The FTO/TiO₂/CdS electrodes were subjected to polarization for 10 min at 50 V in CZTS or CCTS NCs solution, which led to the formation of black colored CCTS and CZTS NCs films on the FTO/TiO₂/CdS electrode. Next, the sulfide/polysulfide electrolyte was prepared by dissolving 0.0329 gm/0.2 M sulfur, 0.237 gm/0.6 M sodium sulfide, and 0.075 gm/0.2 M KCl powders in 5 mL deionized water. The copper sulfide (CuS) counter electrode was prepared by an earlier reported process [31]. Metal



Scheme 1. Facile hot-injection method setup for the synthesis of CZTS and CCTS NCs.

contacts were made using indium wire, which were soldered on the FTO surface and employed as working and counter electrodes for the collection of charges. Finally, the devices with architectures FTO/TiO₂/CdS/CZTS/ZnS/S⁻/S_n⁻/CuS/FTO and FTO/TiO₂/CdS/CCTS/ZnS/S⁻/S_n⁻/CuS/FTO were prepared by sandwiching the photo-anode (FTO/TiO₂/CdS/CZTS/ZnS) and counter electrode (CuS/FTO) using 50 μ L electrolyte (S⁻/S_n⁻). A spacer is used to avoid a short circuit between the photo-anode and counter electrode. The solar cells were then sealed using binder clips prior to efficiency measurements.

2.4. Characterization

The CZTS and CCTS NCs were characterized by several experimental techniques. X-ray diffraction (XRD) pattern were recorded by an X-ray diffractometer (Bruker D8 Advance, Germany). Raman spectroscopy data were obtained by He-Ne laser at 532 nm wavelength with the resolution of 1 cm^{-1} . During measurements, the power of the Raman laser was kept at less than 5 mW. High resolution transmission electron microscopy (HR-TEM) (TECNAI G2-20-TWIN) was used to obtain high resolution micrographs and selected area electron diffraction (SAED) patterns. X-ray photoelectron spectroscopy (XPS) was performed on the CZTS and CCTS samples with a Kratos Axis Ultra DLD photoelectron spectrometer, utilizing monochromatic AlK α radiation operating at an energy of 120 W. XPS data was analyzed using CasaXPS processing software. All XPS spectra were calibrated to the C (1 s) line, taken to be 284.8 eV. The optical band gap was determined from absorbance spectra, measured using a JASCO, V-670 UV-Visible spectrophotometer in the range of 300–1600 nm. The photovoltaic characteristics of the CCTS and CZTS films were studied using a solar simulator system using an AM 1.5 G spectrum with an illumination density of 100 mW/m^2 at 25 $^{\circ}\text{C}$.

2.5. Computational details

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna ab-initio simulation package (VASP) [32–34] with the projector-augmented wave (PAW) method and a plane-wave cut-off of 350 eV. For the PAW potentials the valence electronic configurations used were 5s²4d¹⁰ for Cd, 4s²3d¹⁰ for Zn, 4s¹3d¹⁰ for Cu, 5s²5p² for Sn, and 3s²3p⁴ for S. The general gradient approximation (GGA) for the exchange-correlation (XC) functional was employed within the Perdew-Burke-Ernzerhof parametrization revised for solids (PBEsol) [35]. Long-range dispersion corrections were included using the D3 approach of Grimme et al.[36] The conjugate gradient method was used for structural optimisations, with the total

energy and force convergence criteria set to 10⁻⁵ eV and 0.01 eV/Å. The Brillouin zone was sampled with a 5 × 5 × 3 Γ -centred Monkhorst-Pack mesh [37]. Suitable band paths compatible with crystal space group symmetry were identified using SeeK-path [38,39]. The distinct initial crystal structure for Kesterite CZTS and Stannite CCTS were taken from Hall et al. experimental measurements.[40] Lattice dynamics calculations were carried out within the harmonic approximation, using the PHONOPY package [41–43] to construct and evaluate the dynamical matrix. The finite displacement method (or the supercell approach) was used to construct the force constants. Vibrational frequency calculations presented were performed using the all-electron code CRYSTAL (2017 release) [44,45] with the hybrid B3LYP exchange-correlation functional [46,47]. The fraction of exact change (α) used in the hybrid functional was determined self-consistently (as the inverse of the dielectric constant) using the method by Skone et al.[48], with the dielectric constants determined using the coupled-perturbed Kohn-Sham method [49]. This self-consistent hybrid functional approach (SC-B3LYP) gave exact exchange percentages of 14.9949% ($\alpha = 0.1499$) for CZTS and 13.6063% ($\alpha = 0.1361$) for CCTS. The computed (averaged) dielectric constant ϵ is 6.675 for CZTS and 7.355 for CCTS. Various combinations of Gaussian-type basis sets available from the CRYSTAL library (<https://www.crystal.unito.it/basis-sets.php>) were tested in order to reproduce the geometry and electronic properties of CZTS and CCTS accurately. Long distance dispersion corrections were invoked using the D3 approach recently implemented in CRYSTAL [36,50,51]. The optimal basis sets taken (unmodified) were: all-electron Peintinger-Oliveira-Bredow triple- ζ -valence + polarization (pob-TVZP) for Cd by Laun et al.[52], TZVP for Zn from Karttunen et al.[53], TZVP for Cu from Linnera et al.[54,55], effective core pseudopotential (SC-ECP) for Sn derived by Metz et al.[56], and 8–6311 G* for S by Bredow et al [57]. In CRYSTAL, the convergence of the real-space summation of the Coulomb and exchange contributions to the Hamiltonian matrix is controlled by five overlap criteria. The values used in this study were 10⁻⁷, 10⁻⁷, 10⁻⁷, 10⁻⁹, and 10⁻³⁰. For the compounds of interest, the convergence with respect to k-points was checked. A Monkhorst-Pack mesh of 7×7×7 was used to sample the first Brillouin zone for both materials [44]. Relative Infra-red and Raman intensities were computed analytically, based on coupled-perturbed Hartree-Fock/Kohn-Sham (CPHF/KS) treatments implemented in the code [58–60].

3. Result and discussion

3.1. Structural properties of CZTS and CCTS NCs

X-ray diffraction (XRD) measurements of CZTS and CCTS NCs were carried out to investigate the crystal phase. Fig. 1(a) shows the

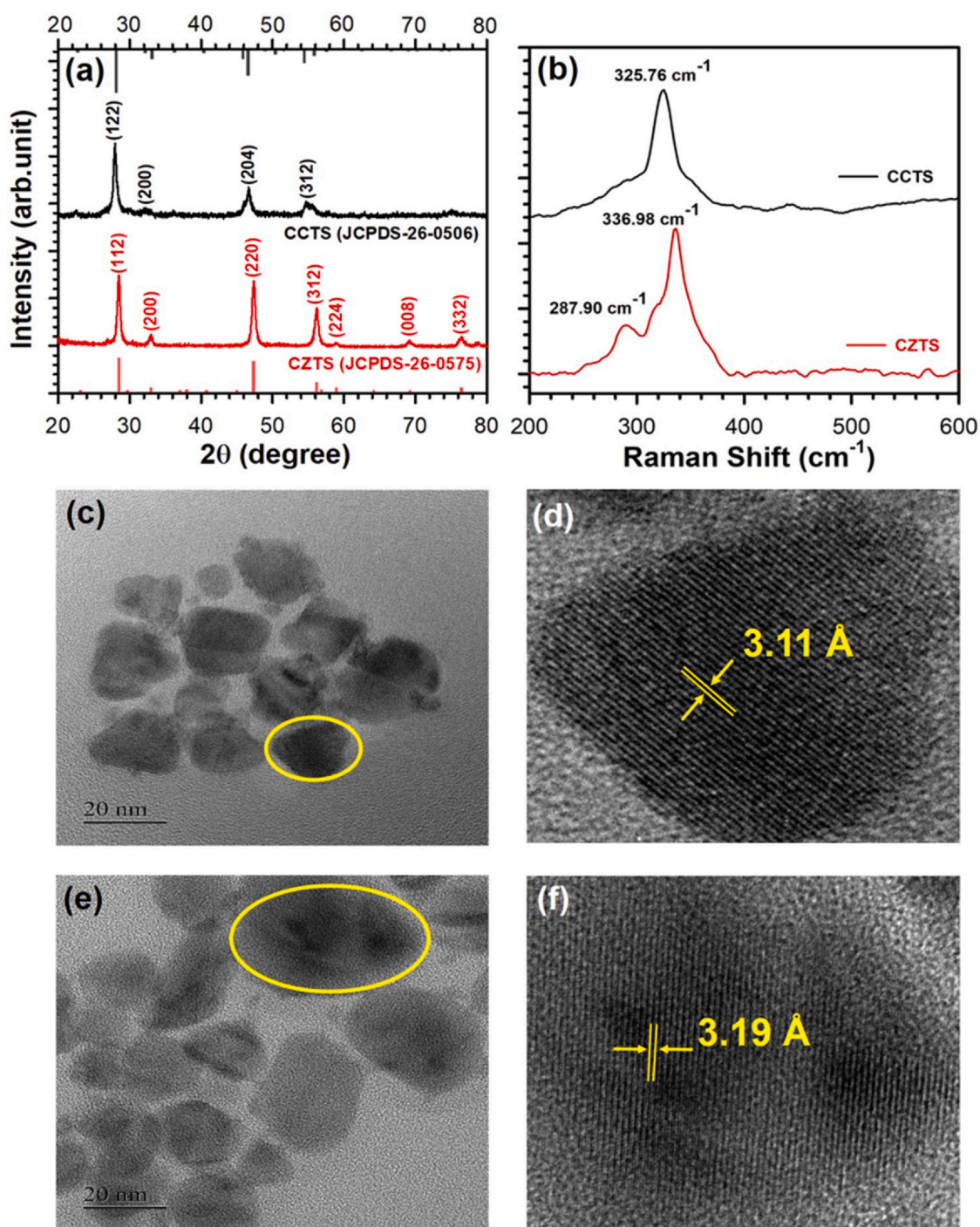


Fig. 1. (a) XRD pattern (b) Raman spectrum for the CZTS and CCTS NCs. Low-resolution TEM images (c, e) and HR-TEM images (d, f) recorded for CZTS and CCTS NCs, respectively.

XRD pattern of the CZTS and CCTS NCs. The CZTS NCs are present in the kesterite phase (JCPDS No. 26-0575, space group $I\bar{4}$, number 82), which shows diffraction peaks at 28.48° , 32.98° , 47.38° , 56.2° , 58.78° , and 69.13° corresponding to the (112), (200), (220), (312), (224), and (332) planar orientations, respectively [28]. The CCTS NCs are present in the stannite (cernyfit) phase (JCPDS No. 26-0506) and show diffraction peaks at 27.94° , 32.2° , 46.66° , 54.7° , which correspond to the (112), (200), (204), and (312) planes, respectively [24]. As observed in previous reports, the shift of the (112) plane in XRD peak from $2\theta = 28.48^\circ$ for CZTS NCs to $2\theta = 27.94^\circ$ for CCTS NCs, confirms the replacement of Zn^{2+} with Cd^{2+} [23]. The average crystallite size, interplanar distance, strain, dislocation density, and lattice

parameters of the CZTS and CCTS NCs are calculated from XRD spectra and reported in Table 1. Raman spectroscopy was carried out to confirm the phase purity of the as-synthesized CZTS and CCTS NCs as shown in Fig. 1(b). The major peak at 336 cm^{-1} and shoulder peaks at 287.90 cm^{-1} correspond to the B_1 and A_1 mode of CZTS, which are consistent with previous literature reports.[24] For the CCTS NCs, the main Raman peak at 325 cm^{-1} corresponds to the symmetric vibrational motion of a sulphur atom in the CCTS crystal structure, which confirms that no impurity phases are present in the CCTS NCs. The observed shift in the Raman spectra of CZTS (336 cm^{-1}) and CCTS (325 cm^{-1}) NCs is due to the exchange of Cd with Zn, which confirms a structural transition from $I\bar{4}$ kesterite to $I4_2m$ stannite, as

Table 1
Lattice parameters of CZTS and CCTS calculated using XRD pattern.

No.	Sample	D (nm)	d_{hkl} (Å)	Strain (ϵ_{hkl})	Dislocation density (ρ) (m^{-2})	Lattice parameter (Å)
1)	Cu_2ZnSnS_4	22.7	3.13	6.70×10^{-3}	1.94×10^{15}	$a = b = 5.41, c = 10.88$
2)	Cu_2CdSnS_4	19.4	3.19	7.19×10^{-3}	2.65×10^{15}	$a = b = 5.53, c = 11.2$

was observed in the XRD patterns.[23,24] The low-resolution TEM images in Fig. 1(c and e) show that the CZTS and CCTS NCs exhibit faceted shapes with diameters ranging from 15 to 35 nm. The high-resolution TEM (HR-TEM) pattern in Fig. 1(d and f) indicates that the NCs have lattice fringes with interplanar distances (d) of 0.311 nm and 0.319 nm, which match the (112) crystal planes of CZTS and CCTS NCs, respectively. It is clearly noticeable from the low resolution TEM images that CZTS and CCTS NCs have different orientations, which are marked by yellow circles in Fig. 1(c and e). This further confirms that both CZTS and CCTS NCs are polycrystalline in nature.

3.2. Density functional theory (DFT)

CZTS and CCTS crystallize in a tetragonal crystal structure in kesterite and stannite phases, respectively. The unit cell contains two formula units in which each atom is found in a tetrahedral environment. The calculated lattice parameters are listed in Table 2. Overall, both utilized approximations for the exchange-correlation functional yield results that are in satisfactory agreement with experimental values (lattice parameters, a (Å) and c (Å)), with the self-consistent hybrid functional showing smaller discrepancies. The tetragonal (kesterite) cell of CZTS (space group $I\bar{4}$, number 82) contains 16 atoms; its 48 vibrational modes can be further classified according to the irreducible representation of the $\bar{4}$ point group as follows:

$$\Gamma_{total} = 3A \oplus 7B \oplus 7^1E \oplus 7^2E.$$

A, B, and E (doubly degenerate) are Raman active modes, while B and E (doubly degenerate) are IR active. The tetragonal (stannite) cell of CCTS (space group $I\bar{4}2m$, number 121) contains a total of 16 atoms, giving rise to 48 vibrational modes which further can be classified according to the irreducible representations of the $\bar{4}2m$ point group as follows:

$$\Gamma_{total} = 2A_1 \oplus 1A_2 \oplus 2B_1 \oplus 5B_2 \oplus 7E.$$

A_1 , A_2 , B_1 , and E (doubly degenerate) are Raman active, B_2 and E (doubly degenerate) are IR active, and A_2 is silent.

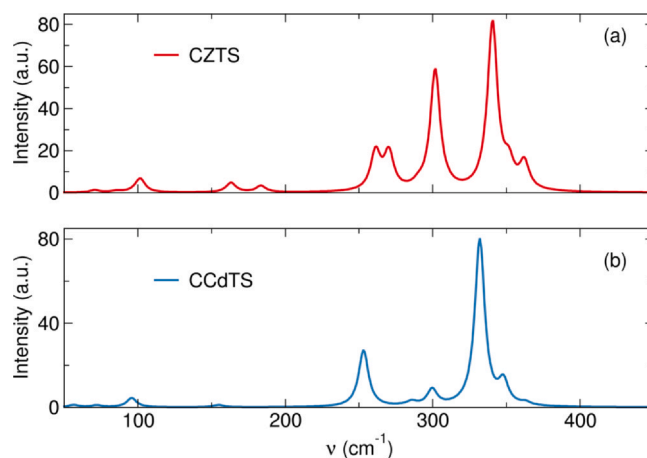
Computed values of the Raman active modes in CZTS and CCTS are reported in Table 3, while the corresponding spectra are shown in Fig. 2 (a and b), respectively. Despite the slight overestimation observed for the Raman mode frequency, the overall spectra are reproduced satisfactorily for both compounds. Graphical animations identify the most prominent (asymmetric) peaks at 340.65 cm^{-1} and 301.70 cm^{-1} for CZTS along with at 331.97 cm^{-1} for CCTS, to originate entirely from a combined stretch-bending S mode. The subsequent most eminent features in the spectra of CZTS, at 261.27 cm^{-1} and 270.25 cm^{-1} (double-degenerate), are attributed to in-plane vibrations and vibrations of all atoms in a disordered pattern, respectively. The eminent mode found at 253.10 cm^{-1} in CCTS (double degenerate, symmetry species E) is assigned to vibrations of all four

Table 2
Lattice parameters of CZTS and CCTS calculated using density functional theory (DFT).

	CZTS		CCTS	
	a (Å)	c (Å)	a (Å)	c (Å)
PBEsol	5.34	10.67	5.49	10.71
SC-B3LYP	5.45	10.88	5.61	10.88
Experiment	[83]	5.42	10.85	5.54
	[40]	5.43	10.87	5.45

Table 3
Calculated Raman properties of powder CZTS and CCTS. The temperature effect was taken for integrated intensities only and the integrated intensities were re-normalized so that the strongest mode is equal to 1000.

CZTS			CCTS		
Symmetry	ν (cm^{-1})	Intensity	Symmetry	ν (cm^{-1})	Intensity
E	70.69	14.30	E	56.25	13.72
B	85.54	8.73	B2	69.67	0.56
B	96.94	4.79	B1	71.99	10.86
E	101.53	82.85	E	95.71	55.56
E	163.14	57.59	B2	151.48	1.40
B	183.46	38.25	E	154.77	12.21
B	261.28	230.43	E	253.10	339.34
E	270.25	220.80	B2	278.99	2.53
A	290.23	25.97	E	285.84	24.00
A	301.70	724.37	A1	299.50	72.31
E	309.82	6.50	B1	300.10	25.54
B	335.15	21.96	A1	331.97	1000.00
A	340.65	1000.00	E	347.96	135.39
E	351.69	135.14	B2	363.11	16.34
B	362.17	157.95			

**Fig. 2.** Calculated Raman spectra of powder polycrystalline (a) CZTS and (b) CCTS. The reported spectra include temperature effects for the integrated intensities only and were re-normalized to the most prominent mode.

atoms, with the strongest contribution coming from the S and Cu atoms. The calculated phonon dispersion across the first Brillouin zone together with the atom projected partial phonon densities of state (DOS) for CZTS and CCTS are shown in Fig. 3 (a and b), respectively. No imaginary modes (negative frequencies or soft modes) were found throughout the first Brillouin zone, satisfying the crystal stability condition which states that the lattice needs to be stable with respect to any small atomic displacement.[61] This means that both compounds are stable at ambient pressure. Replacing Zn with Cd, however, does introduce more phonon states at lower frequencies (pDOS graph), around 1.75 THz. However, those do not induce strong acoustic mode softening to drive a dynamic instability of CCTS.

3.3. Oxidation state and compositional analyses of CZTS and CCTS NCs

The electronic and chemical properties of CZTS and CCTS materials are confirmed from XPS. Fig. 4 shows the XPS spectrum for the

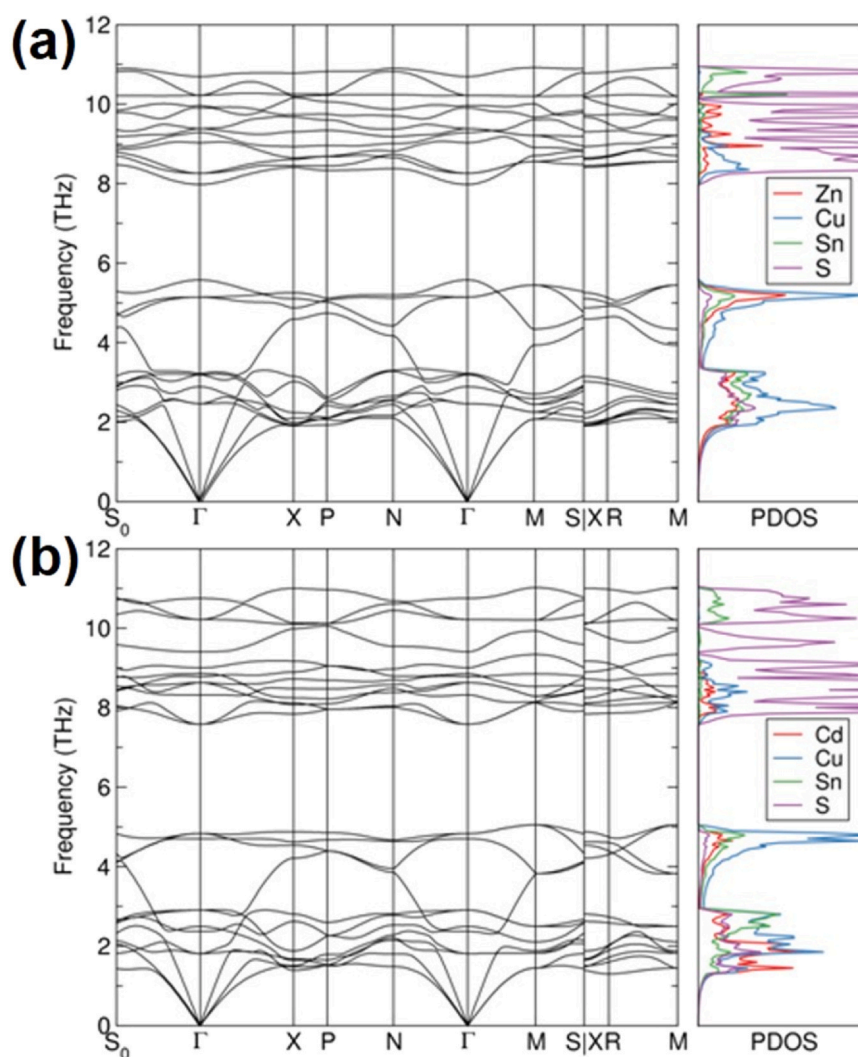


Fig. 3. Full phonon dispersion curves and the corresponding atom-projected partial phonon densities of state for CZTS and CCTS.

as-synthesized CZTS (left panel) and CCTS (right panel) NCs, respectively. All the spectra are deconvoluted via a Voigt curve fitting function in the Shirley background. The high-resolution XPS spectrum in Fig. 4(a) shows 4 well-defined peaks of Cu($2p_{3/2}$), shake-up satellite of Cu($2p_{3/2}$), Cu($2p_{1/2}$), and shake-up satellite of Cu($2p_{1/2}$), sequentially. Furthermore, deconvolution of Cu(2p) shows a perfect fit for 8 peaks of Cu $^{2+}$ ($2p_{3/2}$), Cu $^{3+}$ ($2p_{3/2}$), shake-up satellite of Cu $^{2+}$ ($2p_{3/2}$), shake-up satellite of Cu $^{3+}$ ($2p_{3/2}$), Cu $^{2+}$ ($2p_{1/2}$), Cu $^{3+}$ ($2p_{1/2}$), shake-up satellite of Cu $^{2+}$ ($2p_{1/2}$), and shake-up satellite of Cu $^{3+}$ ($2p_{1/2}$) located at binding energies of 933.22(≡a), 936.39(≡a'), 941.15(≡b), 944.87(≡b'), 953.07(≡c), 956.37(≡c'), 961.05(≡d), and 964.11(≡d'), respectively. The double peak features of Cu(2p) and their accompanying shake-up satellite peaks illustrate the existence of Cu $^{2+}$ ions and an open 3d 9 shell of Cu $^{2+}$ [62,63]. The energy separation of 19.85 (± 0.05) eV observed between Cu $^{2+}$ ($2p_{3/2}$) and Cu $^{2+}$ ($2p_{1/2}$), and their shake-up satellite peaks, is assigned to the formation of Cu $^{2+}$, and not of Cu 0 or Cu $^{1+}$ [63]. The deconvolution of the XPS spectrum of Cu(2p) in Fig. 4(e) illustrates the presence of Cu $^{2+}$ ions in the CCTS NCs, and they are similar to the peak positions of CZTS NCs in Fig. 4(a). Furthermore, the Zn(2p) XPS spectrum (Fig. 4(b)) shows the double peaks of Zn($2p_{3/2}$) and Zn($2p_{1/2}$) located at binding energies of 1023.28 and 1046.18 eV, respectively, with an energy separation of 22.9 eV, which reveals the appearance of Zn $^{2+}$ ions in the CZTS NCs. The Zn($2p_{3/2}$) peak position is relatively higher than the values reported for ZnS (i.e., 1021.2 eV),[64] ZnO

(i.e., 1020.8–1022.58 eV),[65] and pure metallic Zn (i.e., 1021.00–1021.58 eV) [65,66], indicating that Zn forms ZnS as the intermediate phase. The double peak feature of Cd(3d) in Fig. 4(f) is deconvoluted into two peaks of Cd($3d_{5/2}$) and Cd($3d_{3/2}$) located at binding energies of 405.76 and 412.51 eV, respectively, with an energy separation of 6.75 eV, which confirms the existence of Cd $^{2+}$ ions in the CCTS NCs. The Cd($3d_{5/2}$) peak position is observed at a ~1–2 eV higher binding energy than that reported for CdS thin films and nanoparticles (i.e., 403.75–404.88 eV) [67–69]. This shift in binding energy in CCTS is akin to our observation in the CZTS NCs and may be ascribed to the existence of Cd in the surrounding of Cu and Sn. The deconvolution of Sn(3d) shows the perfect fit for two peaks of Sn($3d_{5/2}$) and Sn($3d_{3/2}$) located at binding energies of 487.37 (± 0.10) (≡ a) eV and 495.78 (± 0.12) (≡ b) eV, respectively, which in both CZTS (Fig. 4(c)), and CCTS (Fig. 4(g)), NCs, are assigned to Sn $^{4+}$ ions. The Sn($3d_{5/2}$) peak position observed at a ~2.4 eV higher binding energy than that of Sn 0 (i.e., 485.0 eV) ruled out the existence of unreacted Sn in CZTS NCs. However, the shoulder peaks at binding energies of 485.72 (≡a') and 494.13 eV (≡b') are observed for CCTS NCs. The intensity of these peaks is relatively inferior to those assigned to Sn $^{4+}$ ($3d_{5/2}$) and Sn $^{4+}$ ($3d_{3/2}$), indicating only negligible existence of metallic Sn 0 . [70] An energy separation of ≥ 8.4 eV is observed for both the samples. Likewise, the deconvolution of the XPS spectra for S(2p) shows the reasonable fit for three peaks located at binding energies of 162.47 (± 0.33), 163.78 (± 0.33) and

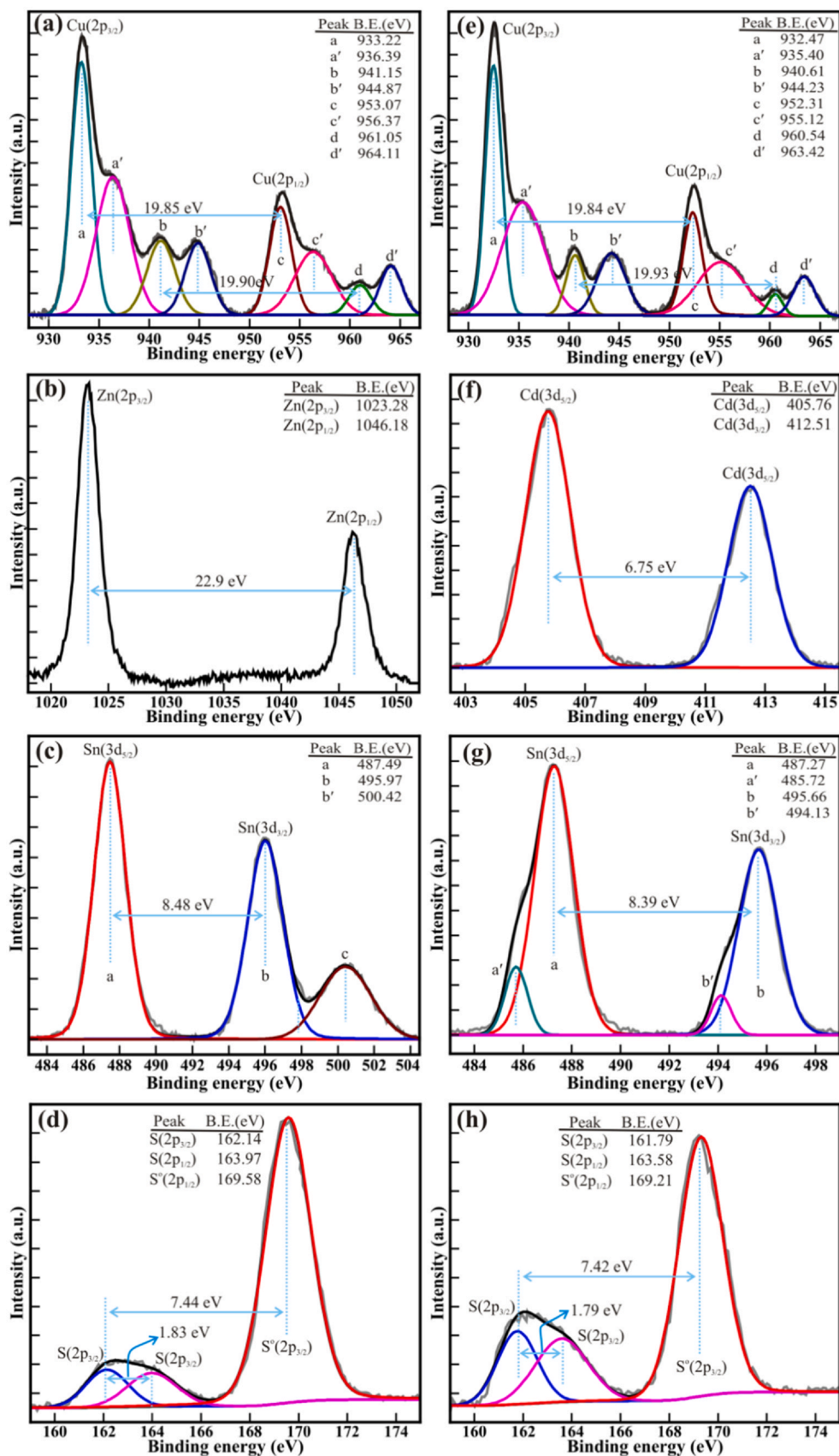


Fig. 4. High-resolution XPS spectra of (a) Cu(2p), (b) Zn(2p), (c) Sn(3d), and (d) S(2p) core levels of CZTS NCs, and (e) Cu(2p), (f) Cd(3d), (g) Sn(3d), and (h) S(2p) core levels of CCTS NCs. All the XPS spectra are deconvoluted with Voigt curve fitting function in the Shirley background.

169.40 (± 0.18) eV for CZTS (Fig. 4(d)) and CCTS (Fig. 4(h)) NCs. The peaks $S(2p_{3/2})$ and $S(2p_{1/2})$ assigned to the binding energies of 162.47 (± 0.33), and 163.78 (± 0.33) confirm the formation of a S^{2-} anion [69,71]. The energy separation of 1.80 (± 0.02) eV observed between $S(2p_{3/2})$ and $S(2p_{1/2})$ is akin to the values reported in the literature and may be attributed to the existence of completely sulfurized CZT and CCdT NCs [70,71]. The peak at a higher binding energy of 169.40 (± 0.18) eV is assigned to SO_4^{2-} , indicating the existence of sulfate species at the surface of both CZTS and CCTS NCs. Overall, the XPS analyses confirm the formation of pure-phase CZTS and CCTS NCs without the growth of undesired phases, or oxidized phases. Most importantly, the replacement of Zn by Cd does not significantly alter the chemical and electronic properties of the Cu, Sn, and S elements in the CCTS NCs.

3.4. Optical properties of CZTS and CCTS NCs

The experimental room-temperature absorbance UV-Vis-NIR spectra of CZTS and CCTS are shown in Fig. 5(a). The spectra reveal photo-absorption in the entire visible region with a tail extending to the near-IR (NIR) region. The Tauc plot for both NCs (insert in Fig. 5(a)) was used to estimate the band gap based on the allowed direct inter-band transitions. The optical band gap of CZTS and CCTS were found to be 1.51 eV and 1.10 eV, respectively. The band gap of CCTS is close to the optimum bandgap for single-junction devices under 1-sun radiation, indicating that CCTS material holds promise for photovoltaic applications.

3.5. Nanocrystals sensitized liquid junction solar cell

Fig. 5(c) is the schematic diagram of the photovoltaic device fabricated with CZTS and CCTS NCs in the FTO/TiO₂/CdS/CZ(Cd)TS/ZnS/S²⁻/S_n⁻/CuS/FTO architecture with 0.25 cm² active area. To

investigate the photovoltaic properties of the CZTS and CCTS NCs sensitized solar cells, we measured their J-V curves under AM 1.5 G illumination. The measured open-circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF) and efficiency (η) for CZTS NCs sensitized solar cells are found to be 0.22 V, 2.48 mA/cm², 0.44%, and 0.25%, respectively (Fig. 5(b) and Table 4), whereas for the CCTS NCs sensitized solar cell, the V_{oc}, J_{sc}, FF, and η values are found to be 0.35 V, 7.50 mA/cm², 0.43%, and 1.16%, respectively (Fig. 5(b) and Table 4). The significant improvement in the V_{oc} and J_{sc} parameters of the CCTS NCs sensitized solar cell can be attributed to its increased light harvesting ability and improved electron transport. The proposed schematic diagram shows the flow of photo-generated electrons and holes in the device as depicted by the arrows in Fig. 5(d). Further improvements in performance could be achieved by increasing grain size, improving structural order to obtain a sharper absorption edge, and reducing the density of defects in the film. It has been reported that sulfurization has led to an increase in grain size and more stoichiometric and structural order [72–74]. The use of annealed CZTS films as the light absorbing layer have shown improved efficiencies compared to the non-annealed films [75–78]. There are variety of reported chemical treatments which have been shown to improve the efficiency [79–81]. Although in the present investigation the obtained device efficiency is low, it is important to note that the absorber layers were not further processed after deposition with any high-temperature or chemical treatments. Hence, further optimization of the synthesis and device fabrication could lead to improved device characteristics. Bai et.al reported 0.19% efficiency using the hydrolysis approach.[20], and also with hydrolysis, CZTS QDSSCs achieved an impressive conversion efficiency of 3.29% with a high short-circuit current of 17.48 mA/cm². [20] Ji et.al. reported 1% efficiency for a CZTS based QDSSC solar cell with a route to phase controllable Cu₂ZnSn(S_{1-x}Se_x)₄ NCs [82]. To the best of our knowledge, this study is the first report of the power conversion efficiency

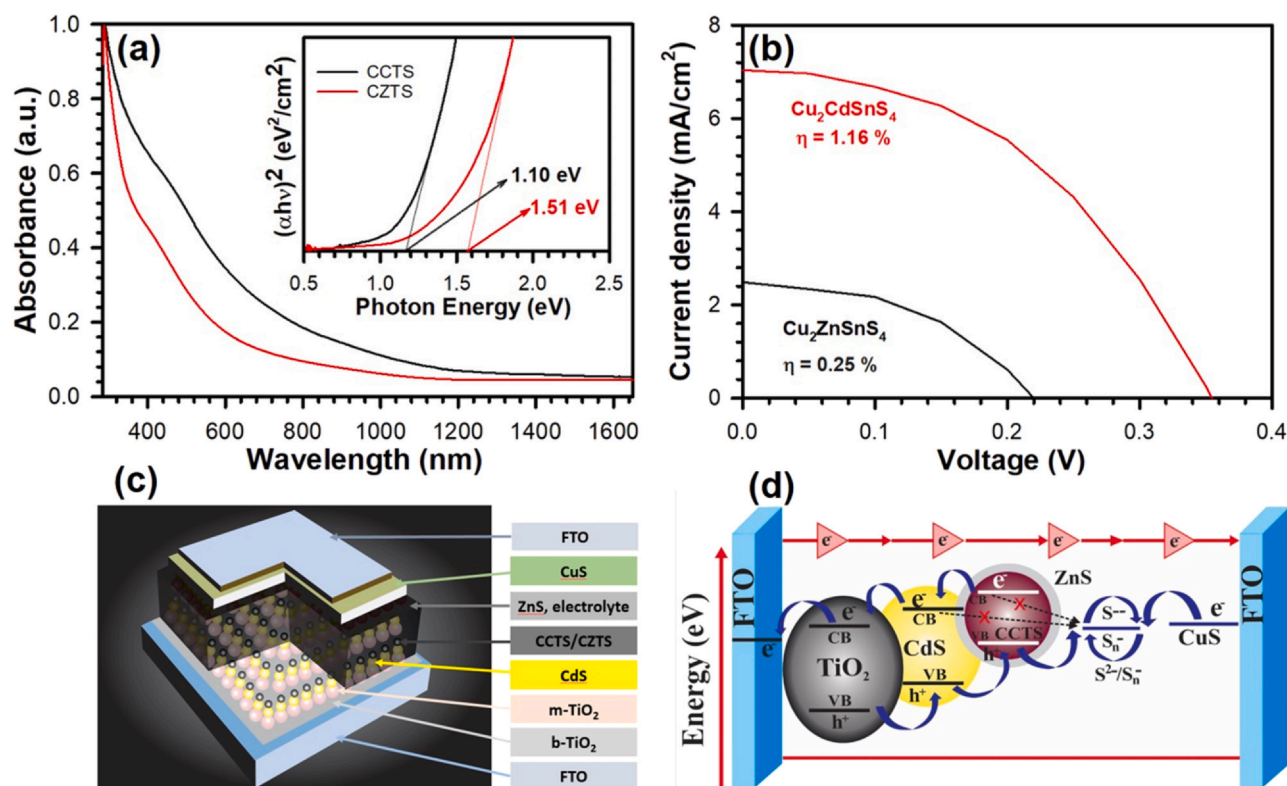


Fig. 5. (a) The UV-Vis-NIR absorbance spectra for CZTS and CCTS NCs with the inset showing the Tauc plot. (b) CZTS and CCTS NCs device architecture: FTO/TiO₂/CdS/CCTS/ZnS/S²⁻/S_n⁻/CuS/FTO. (c) Photovoltaic (J-V) characteristics of CZTS and CCTS NCs solar cells. (d) Schematic diagram for operating principle of a nanocrystal sensitized solar cell, solid arrows represent charge carrier transfer paths, whereas dotted lines indicate paths for detrimental back electron transfer.

Table 4
Device performance, crystal structural parameters along with the elemental composition.

Material	Device Parameters	Device Performance	Composition Properties	Atomic Percentage (%)
Cu ₂ ZnSnS ₄	Fill factor (FF)	0.44	Copper (Cu)	11.41
	Current density (J _{sc})	2.48 mA/cm ²	Zinc (Zn)	3.62
	Open circuit voltage (V _{oc})	0.22 V	Tin (Sn)	5.07
	PCE (η)	0.25%	Sulfur (S)	19.30
Cu ₂ CdSnS ₄	Fill factor (FF)	0.43	Copper (Cu)	14.89
	Current density (J _{sc})	7.50 mA/cm ²	Cadmium (Cd)	6.32
	Open circuit voltage (V _{oc})	0.35 V	Tin (Sn)	7.81
	PCE (η)	1.16%	Sulfur (S)	29.07

(PCE) > 1% for a CCTS NCs sensitized solar cell. Further work in optimization of device fabrication is expected to increase the efficiency of CCTS NCs sensitized solar cell. Specifically, for the FTO/TiO₂/CdS/CCTS/ZnS/S⁻/S_n⁻/CuS/FTO device architecture, optimization of each layer thickness and interface will reduce carrier trapping and should be addressed in future investigations.

4. Summary and Conclusion

We have successfully synthesised Cd-substituted CZTS NCs (CCTS) using the hot-injection method and highlighted the advantages of Cd incorporation in CZTS for nanocrystal sensitized liquid junction solar cell fabrication. Highly crystalline phase-pure CZTS and CCTS NCs were obtained in the kesterite and the stannite phases, respectively, and a bandgap reduction from 1.51 eV (CZTS) to 1.1 eV (CCTS) was demonstrated. Consistent with its optimum band gap, the fabricated CCTS NCs sensitized solar cell shows superior device characteristics (V_{oc} = 0.35 V, J_{sc} = 7.50 mA/cm⁻², FF = 0.43, and η = 1.16%) than that of the equivalent CZTS device. This work should prompt further investigations to obtain the controlled synthesis of solution-processed CCTS NCs with improved structural and optoelectronic properties, lower defect density, along with optimized p-n junction device structures to achieve improved PV performance.

CRediT authorship contribution statement

S.R.R., S.R.J., and N.Y.D. contributed to the conception and design of the experiments. S.R.R. and Y.A.J. completed all the samples synthesis. S.B.J., G.K.R., A.V.R., R.S.D., S.K., and R.L.Z.H. conducted most of the characterizations. A.Z., R.W.C., N.H.D.L., and N.Y.D. carried out DFT analysis and discussed results. S.R.R., H.N.G., and N.Y.D. participating the writing the manuscript and discussed results. All authors discussed the results, contributed to manuscript write-up, and reviewed the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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of ARCHER (<http://www.archer.ac.uk>), the UK's national super-computing service via the membership of the UK's HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202). Information on the data that underpins the results presented here, including how to access them, can be found in the Cardiff University data catalogue at <http://doi.org/10.17035/d.2021.0139534729>.

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