Research Article

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Fabrication, characterization, and photocatalytic performance of ternary cadmium chalcogenides CdIn\textsubscript{2}S\textsubscript{4} and Cd\textsubscript{7.23}Zn\textsubscript{2.77}S\textsubscript{10}-ZnS thin films

Abstract: Dithiocarbamate complexes \([\text{Cd(S\textsubscript{2}C\textsubscript{y}C\textsubscript{y}C\textsubscript{y}\textsubscript{2})\textsubscript{2}(py)}](1)\), \([\text{In(S\textsubscript{2}C\textsubscript{y}C\textsubscript{y}C\textsubscript{y}\textsubscript{2})\textsubscript{3}‧2py}(2)\) and \([\text{Zn(S\textsubscript{2}C\textsubscript{y}C\textsubscript{y}C\textsubscript{y}\textsubscript{2})\textsubscript{2}(py)}](3)\) were synthesized and toluene solution of (1) and (2) was used as dual source precursor for the synthesis of CdIn\textsubscript{2}S\textsubscript{4} (CIS), while that of (1) and (3) was applied for the deposition of Cd\textsubscript{7.23}Zn\textsubscript{2.77}S\textsubscript{10}–ZnS composite (CZS-ZS) thin film photoanodes by employing single step aerosol assisted chemical vapor deposition (AACVD) technique. Deposition experiments were performed at 500°C under an inert ambient of argon gas. The structural properties of deposited films were evaluated by using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The field emission scanning electron microscopy (FESEM) exposed surface morphologies while UV-Visible spectrophotometry revealed that CIS is low band gap photoanode in comparison to CZS-ZS. The comparison of photoelectrochemical (PEC) responses measured in identical conditions in terms of linear sweep voltammetry (LSV) depicts photocurrent density of 4.4 mA/cm\textsuperscript{2} and 2.9 mA/cm\textsuperscript{2} at applied potential of 0.7 V under solar light intensity of 100 mW/cm\textsuperscript{2} for CIS and CZS-ZS respectively. Further, electrochemical impedance spectroscopy (EIS) confirms that PEC properties of CIS are superior to CZS-ZS photoanode as the former offer less charge transfer resistance (R\textsubscript{ct}) 0.03 MΩ in comparison to CZS-ZS having R\textsubscript{ct} value of 0.06 MΩ.

Keywords: CdIn\textsubscript{2}S\textsubscript{4}, Cd\textsubscript{7.23}Zn\textsubscript{2.77}S\textsubscript{10}–ZnS composite, photoanode, photovoltaic, PEC, R\textsubscript{ct}

1 Introduction

Several different methods such as electrolytic, thermochemical, direct solar water splitting, biological processes and steam methane reforming have been developed for commercial production of hydrogen for utilization as clean energy source (Dou et al., 2019; Kim et al., 2018; Sapountzi et al., 2017; Singh and Wahid, 2015; Thalluri et al., 2020). Among these methods the solar water splitting process has a great potential for the future benign energy source (Acar et al., 2016; Dincer, 2012). Because of crucial role of photocatalyst in water splitting to oxygen and hydrogen, a large variety of materials belonging to different classes of compounds have been tested, but unfortunately none of the materials could be found suitable that would stand harsh water oxidation conditions. The single metal sulphides such as PbS, CdS and CuS are widely used photocatalysts due to their suitable band gaps which enables them to capture the profuse part of solar light (Cheng et al., 2018; Mamiyev and Balayeva, 2015; Meng et al., 2013). But these are susceptible to photo corrosion due to greater redox potential of sulphur than oxygen which greatly limits their utilization as photocatalyst. Efforts to manage this problem were made by structuring heterojunction, stacking on supportive materials, mixing of other ingredients and primarily by interlayer incorporations, but all these incorporating steps could lead to poor photocatalytic performance (Liu et al., 2019). Recently bimetallic chalcogenides are getting great attention due to their strong visible light absorption and...
Cadmium zinc sulphide (CdZnS) with varying amounts of Cd and Zn, is another bimetallic chalcogenide which is widely used as windows in heterojunction solar cells to increase their efficiency (Chu et al., 1991; Hussain et al., 1991; Reddy and Reddy, 1992). It is of great technological curiosity mainly because of tuneable band gap even by small change in Zn contents which allows its usage in short wavelength optoelectronic device, LED’s, laser diodes, photodetectors and memory devices (Lee et al., 2002; Redwan et al., 2003; Wu et al., 1993). CdZnS semiconductors are preferred over CdS in photocatalytic water splitting devices for hydrogen production as blending of CdS with ZnS leads to CdS solid solutions which has more negative conduction band decomposed at relatively low temperature. Moreover, the composition of CdZnS also remains intact during PEC performance in comparison to CdS which disintegrates into soluble Cd$^{2+}$ ions, which are toxic and also limit the working of PEC devices (Verma et al., 2015).

In the present work we report the synthesis of CdIn$_S_{x}$ solid solution and Cd$_{1-x}$Zn$_x$S thin film photoanodes via AACVD technique employing dual source toluene solution of dithiocarbamate precursors. The structural features of fabricated photoanodes were evaluated using XRD, Raman spectroscopy, FESEM, EDX, and XPS analysis. The optical analysis presented low band gap energies of CIS than that of CZS-CS. The photoelectrochemical studies interms of LSV and EIS indicate effectiveness of fabricated films in PEC and photocatalytic devices.

## 2 Results and discussion

Dithiocarbamate complexes $[\text{Cd(SCNCy}_3])_{(py)}$ (1), $[\text{In(SCNCy}_3])_{(2py}$ (2), and $[\text{Zn(SCNCy}_3])_{(py)}$ (3) are synthesis via metathetical reactions of sodium dicyclohexylidithiocarbamate with cadmium nitrate, indium trichloride, and zinc chloride respectively, under an inert ambient of argon gas according to the following reactions:

$\text{Cd(NO}_3)_2 + 3\text{H}_2\text{O} + 2\text{Na(SCNCy}_3,\text{py}) \rightarrow \text{Cd(SCNCy}_3\text{C}_6\text{H}_4\text{)}_{(2py)} + 2\text{NaNO}_3 + 3\text{H}_2\text{O}$ \hspace{1cm} (1)

$\text{InCl}_3 + 3\text{Na(SCNCy}_3\text{C}_6\text{H}_4\text{)}_{(2py)} \rightarrow [\text{In(SCNCy}_3\text{C}_6\text{H}_4\text{)}_{(2py)}] + 3\text{NaCl}$ \hspace{1cm} (2)

$\text{ZnCl}_2 + 2\text{Na(SCNCy}_3\text{C}_6\text{H}_4\text{)}_{(2py)} \rightarrow [\text{Zn(SCNCy}_3\text{C}_6\text{H}_4\text{)}_{(2py)}] + 2\text{NaCl}$ \hspace{1cm} (3)

All complexes are obtained in good yield and characterized by m.p., CHNS and FTIR spectroscopical analysis. The IR spectra of complex 1 to 3 exhibit strong absorption bands in wavenumber (ν) region of 1425 to 1496 m$^{-1}$ depicting vibrational modes of C–N bond stretching. These values are intermediate in reported C–N single (1250-1360 cm$^{-1}$) and C=N double bonds (1640–1690 cm$^{-1}$) confirming the bidentate coordination of dithiocarbamate moieties with central metal and partial double bond characteristics of C–N bond. Complex 1 to 3 are synthesized in pyridine solvent. This pyridine gets coordinated with central metals zinc and indium in 1 and 3 while it is present as a solvent molecule in 2. The pyridine containing dithiocarbamate precursors are air stable, easily synthesised, more volatile and conveniently decomposed at relatively low temperature. Moreover, complex 1-3 are easily soluble in common organic solvents and decomposed before 500°C to stable products. Therefore, these are employed as dual source precursors in AACVD technique for the deposition of CdIn$_S_{x}$ solid solution and Cd$_{1-x}$Zn$_x$S$_{10}$–ZnS composite thin films at 500°C.

### 2.1 XRD analysis

To investigate structural parameters like crystallite size, degree of crystallinity, crystalline phase and phase purity, CIS and CZS-ZS thin films were subjected to XRD analysis. The reflection pattern of CIS thin films (Figure 1) produced from toluene solution of precursor (1) and (2) is strongly matched with reported cubic crystalline phase of CdIn$_S_{x}$ [ICDD# 00-027-0060], with space group of Fd3m and cell parameters $a = 10.8450$ Å. The indexed peak positions and lattice planes in purple colour corresponds to CdIn$_S_{x}$ while that in green matches fluorine doped tin oxide (FTO) substrate. One unidentified peak (3-5% impurity)
at 46.60° is most probably due to some side reaction such as reaction of precursors with FTO substrate. Sticky pattern matching with original peak pattern is provided in Figure A1. However, the XRD pattern obtained for CZS-ZS composite thin films (Figure 2) showed that two crystalline phases of $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ and $\text{ZnS}$ are generated from the thermal decomposition of aerosols produced from the respective solution of precursor (1) and (3).

The formation of $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ phase is affirmed by matching lattice reflections with standard card, ICDD# 00-040-0836. The peaks indexed in red colour corresponds to hexagonal crystalline phase of $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ having a space group of $\text{P6}_3\text{mc}$ with cell parameters $a = 4.0420$ Å and $c = 6.5880$ Å. Whereas, the reflections obtained for hexagonal phase of $\text{ZnS}$ are indicated in black colour. It is found that two peaks from both the phases ($\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ and $\text{ZnS}$) are overlapping at 27.33° and 29.07°, which is avowed by increase in peak intensities as compared to the peaks produced by individual species. The remaining peaks labelled in green correspond to FTO substrate. Sticky pattern matching with original peak pattern is available in Figure A2. The crystallite size of CIS (90 nm) and CZS-ZS (110) films was determined by Scherer’s calculator. These XRD outcomes elucidate that CIS films comprises of only a single phase of $\text{CdIn}_2\text{S}_4$ with no extra peaks of $\text{CdS}$ or $\text{InS}_2$, while the other films of CZS-ZS contain two phases of $\text{Cd}_{7.23}\text{Zn}_{2.77}\text{S}_{10}$ and $\text{ZnS}$. However, spectra of both films indicate the high purity and good crystallinity of the end product.

### 2.2 XPS analysis

In order to determine elemental composition and valence states of individual components, synthesized CIS and CZS-ZS thin films were subjected to surface sensitive X-ray photoelectron spectroscopy (XPS). The XPS survey scans of both CIS and CZS-ZS thin films confirms the presence of components in expected ratio as suggested by XRD study. Thin films of the CIS presented Cd, In, and S (1:2:4) while that of the CZS-ZS constitute Cd, Zn, and S (1:2:4) on the surface of FTO. No noticeable peaks for any impurity are observed (Figure 3). Figures 4a-d represent the results of high-resolution XPS analysis, the Cd discloses a 3d doublet state at binding energies of 404.6 eV (Cd 3d$_{5/2}$) and 411.3 eV (Cd 3d$_{3/2}$) in both CIS and CZS-ZS films with separation energy of 6.7 eV, correspond to +2 oxidation states. The narrow scan of Zn furnished a characteristic peak at 1022 eV for Zn 2p, approves the existence of Zn$^{2+}$ in CZS-ZS composite and that of In provided a doublet state at binding energies of 444.1 eV and 451.1 eV corresponding to In 3d$_{5/2}$ and In 3d$_{3/2}$, respectively, with a separation energy of 7 eV, depicting its +3 oxidation state in the CIS.
The narrow scans of sulphur in both CIS and CZS-ZS films showed similar pattern where its prevalence in S\textsuperscript{2} oxidation state in mixed metal sulphides is confirmed by the presence of two peaks with separation of 1.2 eV. These XPS findings of Cd, Zn, In, and S in fabricated films are in accordance with the already reported values (Lopez et al., 2005; Zhang et al., 2013). The atomic ratio of Cd, In, and S in CIS and that of Cd, Zn, and S in CZS-ZS was also found by EDX analysis. All the results showed presence of all target elements in proper ratio (Figure A3).

2.3 Raman studies

The as deposited CdIn\textsubscript{2}S\textsubscript{4} and Cd\textsubscript{7.23}Zn\textsubscript{2.77}S\textsubscript{10}-ZnS composite thin films were subjected to Raman spectroscopic analysis to further investigate their structure at micro-levels and results are depicted in Figure A4. There appears a sharp vibrational mode at 291.9 cm\textsuperscript{-1} and other small modes at 417.7, 582.2, 596.6, 609.5, and 665.2 cm\textsuperscript{-1} in Raman spectra of CIS thin films (Figure A4a). These results can be correlated with Raman studies of CdIn\textsubscript{2}S\textsubscript{4} by Unger et al. (1978), where he compared the results of FT-IR and Raman spectra interns of active and inactive modes. Anyways, these results are quite different from the single crystal Raman results of CdIS probably due to the small size of particles and porous texture. The outcomes of Raman analysis of CZS-ZS thin films are illustrated in Figure A4b, which show five distinct vibrational modes at 306.5, 395.7, 437, 545.5, and 585.9 cm\textsuperscript{-1}. The Raman spectrum for ZnS reported by Kumar et al. (2006) showed that material gave strong absorption modes at 258, 344, 276, and 351 cm\textsuperscript{-1} while that of CdS Raman studies performed by Chawla showed optical phonons at 300 cm\textsuperscript{-1} (1LO) and 600.527 cm\textsuperscript{-1} (2LO). The results obtained in our case are different from reported Raman shifts of pure CdS and ZnS phase that may be attributed to the synergistic effect of Cd and Zn in the Cd\textsubscript{7.23}Zn\textsubscript{2.77}S\textsubscript{10} phase of CZS-ZS composite films (Chawla et al., 2010).

2.4 FESEM analysis

Figure 4 illustrates surface morphologies of CIS and CZS-ZS thin films, determined by using field emission scanning electron microscopy (FESEM). The CdIn\textsubscript{2}S\textsubscript{4} thin films are grown as clusters of spherical balls on FTO at 500°C in 40 min deposition time. These balls vary in size from 2.79 to 3.54 µm, have well defined sharp boundaries and are uniformly distributed on entire surface of substrate as shown in low magnification image (Figure 5a). The inset of Figure 5a reveals that these micro-balls are composed of small repeating units that make their structure porous. Whereas CZS-ZS thin films present irregular size lumps of composite material which also have strong interlinkage and uniform distribution on entire FTO surface. A careful look at FESEM image (Figure 5b) further divulges that it leaves some voids due to dovetailing of these lumps and
Fabrication, characterization, and photocatalytic performance of ternary cadmium porosity in structure is observed. The inset of Figure 5b gives information about size of these lumps which is in 3.47 µm in length and 1.55 µm in width. It also expresses that lumps have well defined sharp boundaries with compact structures. This comparison discloses that both thin films have evenly distributed particles but CdIn$_2$S$_4$ films retain relatively more uniformity in terms of particle shapes and sizes as compared to that of CZS-ZS, which may be attributed due to two distinct phases in the later which was already verified in XRD analysis. But despite of above-mentioned difference, both thin films possess porous texture that reduces their band gap energies and increase visible light harvesting efficiency.

2.5 Optical Studies

The optical absorption and band gap energies of fabricated thin films were determined by using UV-Visible (UV-Vis) spectrophotometer in the wavelength region of 380 to 900 nm. Figure 6a depicts that optical absorbance of CIS films increases smoothly in the wavelength region of 900 to 580 nm followed by an abrupt increase in remaining visible portion. Similarly, CZS-ZS films also absorb light in whole visible zone but this absorption is not smooth as shown in Figure 6b. It is expected that two distinct phases of Cd$_{23}$Zn$_{27}$S$_{16}$ and ZnS in CZS-ZS thin films could not establish synergistic effect and absorb in different region of light and give a non uniform absorbance trend. The direct band gaps are calculated by using Tauc’s equation (Munawar et al., 2019):

$$\alpha \cdot h\nu = A(h\nu - E_g)^n$$

where $\alpha$ is the linear absorption coefficient of the material, $h\nu$ is the photon energy, $A$ is a proportionality constant and $n$ is a constant depending on band gap nature; $n = 1/2$ for allowed direct and $n = 2$ for indirect band gap. The direct band gap was calculated by arranging Tauc’s equation as follows:

$$\alpha \cdot h\nu = A(h\nu - E_g)$$

Figure 5: FESEM images of (a) CdIn$_2$S$_4$ and (b) Cd$_{7.23}$Zn$_{2.77}$S$_{10}$-ZnS composite thin films deposited on FTO substrate and insets are the corresponding high magnification images.

Figure 6: UV-Vis absorption spectra of (a) CIS and (b) CZS-ZS thin films. Insets are the corresponding Tauc’s plot indicating band gap energies.
and results suggested 1.74 eV for CIS and 2.07 eV for CZS-ZS thin film photoanodes as shown in the insets of Figures 5a,b, respectively. These obtained values are less than reported band gap values of CdS (2.45 eV), (2.4-2.45 eV), and Cd$_{7.23}$Zn$_{2.77}$S$_{10}$ (2.57eV) (Mahajan et al., 2017; Zhang et al., 2013). It may be attributed to uniform distribution of well crystalline particles in case of both CIS and CZS-ZS thin films.

### 2.6 Photoelectrochemical studies

Photoelectrochemical response of fabricated CIS and CZS-ZS thin film photoanodes was tested under solar light intensity of 100 mW/cm$^2$ using conventional electrochemical work station of three probe electrodes. The as-synthesized thin films were employed as working electrode, platinum wire as counter electrode and Ag/AgCl in 3 M KCl as reference electrode in 0.01 M Na$_2$S solution as an electrolyte (Mansoor et al., 2017). Linear sweep voltammetry (LSV) results, as shown in Figure 7, clearly depict that both CIS and CZS-ZS thin films offered negligible current under dark conditions, but remarkable photocurrent is obtained when irradiated with 100 mW/cm$^2$ solar light intensity. Interestingly, both CIS and CZS-ZS films displayed similar behaviour towards applied potential and show a uniform elevation with maximum photocurrent density of 4.4 and 2.9 mA/cm$^2$, respectively, at 0.7 V. The improved photoresponse of CIS photoanode vs. CZS-ZS and other previously reported CdIn$_2$S$_4$ photoelectrodes can be correlated to its low band gap energy and homogenous distribution of allied bunches of vertically grown micro balls.

The uniform distribution of particles is mainly responsible for electrode-electrolyte penetration. This linkage helps CIS photoanode to generate and separate the charge carriers (e$^-\cdot$h$^+$) more efficiently relative to CZS-ZS photoanode where composite formation leads different phases to compete for light absorption rather than reducing recombination by synergistic effect due to mismatched band edges. The efficiency of a typical p-type semiconductor largely depends upon the generation, separation, recombination, and transportation of electron-hole pairs. The electron impedance spectroscopic EIS studies were carried out in 0.01 M Na$_2$S solution in frequency range of 0.1 Hz to 10 KHz to investigate charge resistance and charge carrier properties of circuit components. In Nyquist plot (Figure 8), the smaller diameter of semicircles of the CIS and CZS-ZS photoanodes under illumination signifies the reduction in charge transfer resistance as compared to dark conditions. The lowering of R$_c$ under illumination confirms the ease of electron transport. The intersection of semicircles to imaginary axis provides the Rct value of CIS and CZS-ZS photoanodes which is 0.03 MΩ for the former and 0.06 MΩ for the latter. It is believed that the auspicious photoresponse, least charge transfer resistance and low band gap values for CIS and CZS-Cds thin films, developed in present study, make these films an appropriate choice for photocatalytic water splitting.

### 3 Conclusions

In summary, a method has been described for the deposition of thin films of CdIn$_2$S$_4$ solid solution (CIS) and Cd$_{7.23}$Zn$_{2.77}$S$_{10}$-ZnS composite (CZS-ZS) thin films by employing toluene solution of dual source precursor using AACVD technique at 500°C. The structural parameters of fabricated films were explicated by using XRD, EDX, XPS, and Raman spectroscopical analysis. The FESEM
analysis provided an insight about surface morphologies of CIS and CZS-ZS thin films which were grown in the shape of spherical balls and lumps, respectively. The optical study by UV-Vis spectrophotometry revealed that CIS is a low band gap photoanode and furnished 4.4 mA/cm² photocurrent density with low R<sub>s</sub> value of 0.03 Ω than that of CZS-ZS. All the above-mentioned results proved that fabricated CIS and CZS-ZS thin film photoanodes can efficiently be used in photovoltaic and photoelectrochemical cells and can be entrusted with the task to uplift electricity and hydrogen production.

**Experimental**

**Synthesis of [Cd (S<sub>2</sub>CNCy<sub>2</sub>)(py)] (1)**

Precursor 1 was synthesized in a metathetical reaction of sodium dicyclohexylthiodicarbamate with cadmium nitrate in chloroform-pyridine solvent system at room temperature (Ehsan et al., 2012). In a typical experiment, argon gas was passed for 30 min through 250 mL round bottom flask (reaction flask), attached with dropping funnel, reflux condenser and inert gas line, to make its internal atmosphere homogenize prior to introduce the reagents. 1.75 g (6.27 mmol) of Na(S<sub>2</sub>CNCy<sub>2</sub>) was dissolved in 30 mL chloroform solvent and transferred to reaction flask followed by the addition of 0.91 g (3.13 mmol) of Cd(NO<sub>3</sub>)‧3H<sub>2</sub>O. The resulting milky coloured solution was stirred for 30 min and then 30 mL pyridine was added which turned the solution colourless and clear. After 1 h further stirring, solution was filtered and allowed to evaporate slowly at room temperature that furnished colourless crystals of bis-(N,N-dicyclohexylthiodicarbamato) (pyridine)cadmium(II) [Cd (S<sub>2</sub>CNCy<sub>2</sub>)(py)] (1). Yield (82%). Characterization: m.p. 221°C (decomposition), CHNS investigation found for C<sub>43</sub>H<sub>56</sub>CdN<sub>4</sub>S<sub>2</sub>; C, 50.91; H, 6.68; N, 6.37%; close to requires: C, 52.89; H, 6.75; N 6.01%. IR (ν<sub>max</sub> /cm<sup>-1</sup>): 2948s, 2841w, 1618s, 1594s, 1499s, 1465s, 1381s, 1345s, 1265s, 1169s, 1130s, 1025s, 753s, 691w.

**Synthesis of [In(S<sub>2</sub>CNCy<sub>2</sub>)]·2py (2) and [Zn(S<sub>2</sub>CNCy<sub>2</sub>)(py)] (3)**

Following the same procedure precursors (2) and (3) were synthesized. Quantities of the reagents used for (2): sodium dicyclohexylthiodicarbamate (1.75 g, 6.27 mmoles) and indium trichloride (0.44g, 2.08 mmol), yield 80%. Characterization: m.p. 254-259°C (decomposition), Elemental analysis found: C, 56.72; H, 7.84; N, 6.33%; S, 18.55%; C<sub>48</sub>H<sub>58</sub>InN<sub>4</sub>S<sub>2</sub> requires: C, 56.46; H, 7.34; N, 6.71%; S, 18.45%. IR (ν<sub>max</sub> /cm<sup>-1</sup>): 2930s, 2850w, 1578s, 1470s, 1345m, 1376s,1346w, 1302m, 1240s, 1160s, 1107s, 1021s, 964m, 920s, 881s, 746s, 704w, 660m, 602m, 542s.

**Deposition of thin films by AACVD**

The CdIn<sub>2</sub>S<sub>4</sub> solid solution (CIS) and Cd<sub>12</sub>Zn<sub>27</sub>S<sub>40</sub>–ZnS composite (CZS-ZS) thin film photoanodes were synthesized in a single step from dual source precursors on flourine doped tin oxide (FTO) substrate via solution oriented self designed AACVD technique. The toluene solution of precursors (1) and (2) is consumed to develope thin films of CIS while that of precursors (1) and (3) for the deposition of CZS-ZS at 500°C. FTO substrate (surface resistivity 7 Ω/sq size 1 × 2 cm) were cleased in ultrasonic bath with doubled deionized water followed by washing with acetone and ethanol and finally stored in ethanol (Daraz et al., 2019).

For deposition of CIS thin films, equimolar amounts of precursor (1) (0.494 g, 0.701 mmoles) and precursor (2) (0.731 g, 0.701 mmoles) were dissolved in 15 mL toluene in a round bottom flask to give clear solution followed by its transfer into a round bottom flask connected to deposition assembly. This deposition assembly consists of tube furnace, an ultrasonic humidifier and argon gas cylinder. FTO substrates were placed horizontally inside the reactor tube, which is then adjusted inside the tube furnace and desired deposition temperature (500°C) was achieved before aerosols generation. An ultrasonic humidifier (MBH-002, Japan) generated aerosols of precursor’s solution by piezolectric effect inside the round bottom flask. These aerosols are transported into reactor tube by argon carrier gas with flow rate of 100 mL/min. The deposition session took place for 40 min, after that humidifier was shut down and substrates were cooled to room temperature with constant flow of argon gas. The gaseous waste was ventilated in fuming hood during deposition process. Fabrication of CZS-ZS thin films was also carried out by employing same procedure using equimolar solution of precursor (1) (0.494 g, 0.701 mmoles).
and precursor (3) (0.494 g, 0.701 mmoles) in toluene solvent at 500°C. The deposition experiments for both CIS and CZS-ZS thin films were repeated several times to ensure the composition of end products.

Thin films characterization

The structural elucidation terms of surface morphology of the CIS and CZS-ZS thin films was performed on field emission gun scanning electron microscope (FE-SEM, FEI Quanta 400) attached with an energy dispersive X-ray (EDX) spectrometer (INCA Energy 200) operating at an accelerating voltage of 20 kV and a working distance of 9.2 mm. The powder XRD analysis was performed on the PAN analytical, X’Pert High Score diffractometer having an intense monochromatic Cu-Kα radiation of wavelength (A) 1.542 Å, to investigate the crystalline phase and degree of crystallinity. The films were scanned from 10° to 90° in order to get all possible reflection, in a step size of 0.026° at 40 kV accelerating voltage and 40 mA current. In order to estimate surface elemental configuration, fabricated photoanodes were subjected to the XPS analysis, which is carried out by using ULVAC-PHI, Quantera II, having Al Kα monochromatic X-ray radiation of 1486.8 eV. To calibrate binding energy, the C 1s beam of 284.6 eV was used as a reference. The UV-Vis spectra of the synthesized films were recorded on the Lambda 35 Perkin-Elmer UV-Vis spectrophotometer in the wavelength range of 380 to 900 nm with reference to bare FTO substrate. The surface thickness of CIS and CZS-ZS thin films on FTO surface was measured by using KLA Tencore P-6 surface profilometer and it comes out 380 and 400 nm, respectively.

Photoelectrochemical studies

The photoelectrochemical (PEC) potential of fabricated CIS and CZS-ZS thin film photoanodes towards solar light harvesting was investigated by using conventional quartz window electrochemical work station of three electrodes, employing fabricated photoanode as working, platinum wire as auxiliary and Ag/AgCl/3M KCl as reference electrodes respectively. The sacrificial reagent 0.01 M Na₂S aqueous solution was used as an electrolyte to minimize the problem of photocorrosion. The PEC measurements in terms of linear scan voltammetry (LSV) and electron impedance spectroscopy (EIS) were made on a potentiostat Autolab type III (Eco Chemie micro) under the steady state conditions of current and voltage. A solar simulator (AM 1.5 classes A, Solar Light 16S-300) of light intensity 100 mW/cm² was used to illuminate the cells. The effective surface area of the working electrode was 1 cm².

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Appendix

Figure A1: Sticky pattern matching with original peak pattern of CIS thin films (Indexed d-spacing) fabricated via AACVD technique at 500°C.

Figure A2: Sticky pattern matching with original peak pattern of CZS-ZS thin films (Indexed d-spacing) synthesised via AACVD technique at 500°C.
Figure A3: EDX spectra of (a) CdIn$_2$S$_4$ and (b) Cd$_{7.23}$Zn$_{2.77}$S$_{10-ZnS}$ composite thin films developed on FTO at 500°C via AACVD technique.

Figure A4: Raman spectra of (a) CIS and (b) CZSZS-ZNS thin films.

Figure A5: FT-IR spectrum of synthesized precursor 1.
Figure A6: FT-IR spectrum of synthesized precursor 2.

Figure A7: FT-IR spectrum of synthesized precursor 3.