Hexagonal structured \( \text{Zn}(1-x)\text{Cd}_x\text{O} \) solid solution thin films: synthesis, characterization and applications in photoelectrochemical water splitting†

Muhammad Adil Mansoor,† Muhammad Ali Ehsan, Vickie McKee,† Nay-Ming Huang,† Mehdi Ebadi,† Zainudin Arifin,† Wan Jeffrey Basirun† and Muhammad Mazhar†

Hexagonal nanostructured zinc-cadmium oxide \( \text{Zn}(1-x)\text{Cd}_x\text{O} \) where \( x = 0.08, 0.15, \) and \( 0.17 \) solid solution thin films were deposited on FTO coated glass substrates from a common solution of zinc acetate and a newly developed polymeric cadmium precursor by an aerosol-assisted chemical vapour deposition (AACVD) technique. The polymeric cadmium precursor \( [\text{Cd}_3(\text{TFA})_4(\text{OAc})_2(\text{THF})_4]_0 \) (1) was synthesized by the reaction of cadmium(II)acetate dihydrate with trifluoroacetic acid in THF solution and characterized by melting point, microanalysis, FTIR, \( ^1\text{H}-\text{NMR} \), thermogravimetry (TG-DTG) and single crystal X-ray analysis. The deposited thin films were characterized by powder XRD, SEM, EDX and UV-visible spectrophotometry, and tested for photoelectrochemical (PEC) water splitting to hydrogen and oxygen. The effect of various thin film deposition parameters such as solvent type, temperature and electrolyte concentration on PEC properties has been investigated. The SEM analysis illustrated that the morphology of the films changes significantly with the change of the solvent. The films deposited from THF solution have a needle-like appearance scattered vertically on the FTO-coated glass substrate. An optical band gap of 2.40 eV has been estimated by UV-visible spectrophotometry. The current–voltage characterization proved that the nanocrystalline hexagonal structured \( \text{Zn}_0.83\text{Cd}_{0.17}\text{O} \) electrodes exhibit an n-type semiconducting behaviour and the photocurrent was found to be strongly dependent on the deposition solvent, deposition temperature and electrolyte concentration. The maximum photocurrent density of 0.23 mA cm\(^{-2}\) at 0.55 V vs. Ag/AgCl/3 M KCl (−1.23 V vs. RHE) was obtained for the \( \text{Zn}_0.83\text{Cd}_{0.17}\text{O} \) photoelectrode deposited at 500°C for 45 min from 0.5 M solution of (1) and \( \text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} \) in THF.

1 Introduction

Hydrogen is the most desirable source of fuel because it possesses a high energy storage capacity of 120 000 J g\(^{-1}\) as compared to 40 000 for oil and 30 000 for coal\(^6\) and its combustion does not result in pollution of the environment. Hydrogen production by water splitting has been an objective of semiconductor photoelectrochemistry for nearly four decades. The energy difference between the oxygen evolution potential and the hydrogen evolution potential is 1.229 eV at 25°C. Therefore, ideally one would like to have a chemically and optically stable semiconductor, in which the conduction and valence bands are positioned favourably so that they bestride the hydrogen and oxygen evolution potentials. To overcome the overpotential which is mainly associated with oxygen evolution, a semiconductor material with a band gap of 1.8–2.0 eV is preferred.

During the last few years, ZnO and related semiconductors have gained substantial interest in the semiconductor research community. The main focus for the application of ZnO materials is in optoelectronic devices,\(^2\) whereby it is important to modulate the band gap. Doping by other elements is an effective way to adjust the band gap of ZnO.\(^3,4\) Among these doping elements, cadmium is a suitable material for reducing the band gap of ZnO.\(^5,6\) Unfortunately, ZnO and CdO have different crystal structures such as hexagonal and cubic respectively. Moreover, the thermodynamic solubility of Cd in the Zn–CdO
alloy system is quite small i.e. ~2 mol% under thermal equilibrium conditions.7,8 Therefore, it is difficult to grow single-phase hexagonal zinc–cadmium oxide solid solution thin films with high Cd contents. In recent years, a variety of methods such as pulsed laser deposition,9,10 molecular beam epitaxy,11,12 metal–organic vapour-phase epitaxy13,14 and magnetron sputtering15 have been employed to deposit zinc–cadmium oxide alloy thin films. We used an aerosol assisted chemical vapour deposition (AACVD) technique in which the precursor is dissolved in a common organic solvent and an aerosol of the solution is generated ultrasonically to deposit layers of the decomposed material on the target substrates while at the same time ensuring both reproducibility and the presence of all the components of interest in the deposited layer(s).16

Therefore, we focused our attention on the synthesis of zinc–cadmium oxide solid solution using a new oxygen-enriched source of cadmium (1) that is capable of delivering cadmium for the isomorphous replacement of zinc in its hexagonal structure. The non-stoichiometric replacement of Zn atoms by Cd is governed by the particle size of ZnO that in turn controls the band gap and photoelectrochemical properties.

In this article we report an AACVD method for the fabrication of hexagonal structured Zn1−xCd2xO alloy thin films. The effect of various thin film deposition parameters such as deposition solvent, deposition temperature and electrolyte concentration was also investigated along with their photoelectrochemical (PEC) properties.

2 Results and discussion

A polymeric complex of cadmium [Cd3(TFA)4(OAc)2(THF)4]n (1) (TFA = trifluoroacetate, OAc = acetato, THF = tetrahydrofuran) has been synthesized by the partial replacement of the acetato ligand by the more strongly chelating trifluoroacetato ligand in stoichiometric quantities of cadmium(n) acetate dihydrate and trifluoroacetic acid in THF solution as shown in the following chemical equation.

\[
\begin{align*}
\text{n(Cd(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + 4\text{CF}_3\text{COOH})} \\
\text{THF} \rightarrow \text{[Cd}_3(\text{CF}_3\text{COO})_4(\text{CH}_3\text{COO})_2(\text{C}_2\text{H}_5\text{O})_2]_n \\
+ \text{n(4\text{CH}_3\text{COOH} + 6\text{H}_2\text{O})}
\end{align*}
\]

The reaction was started with a molar (1:2) mixture of Cd(OAc)2 - 2H2O and trifluoroacetic acid, with a hope to replace all the acetato ligands with TFA, but the stoichiometry of the complex ascertained by microanalysis, FT-IR,1H and 19F NMR, thermogravimetry and single crystal X-ray diffraction analysis revealed formation of a polymeric product with partial replacement of acetate ligands with TFA. The FT-IR spectrum of complex (1) shows the presence of characteristic vibrations of functional groups attached to the cadmium atoms in (1). The symmetric and asymmetric ν(C=O) vibrations of the acetato and trifluoroacetato ligand have been identified at 1552 and 1415 cm⁻¹ and 1679 and 1442 cm⁻¹ respectively. The difference of 137 and 249 cm⁻¹ between asymmetric and symmetric ν(C=O) vibrations indicates the bidentate nature of the carboxylate groups of the acetato and trifluoroacetato ligands that are bonded to different cadmium centres. Similarly, the peak at 1193 cm⁻¹ confirms the presence of C–F bonds in complex (1). The 1H NMR recorded in DMSO shows two signals at δ = 3.60 ppm [t, 16H, OCH3] and δ = 1.76 ppm [p, 16H, CH3] due to the solvated THF and δ = 1.85 ppm [s, 6H, CH2] due to the acetato group, whereas 19F-NMR recorded in DMSO shows a singlet at δ = −73.60 ppm [s, 12F, CF3] indicating the presence of a trifluoroacetato ligand in complex (1).

2.1 Structural analysis of [Cd3(TFA)4(OAc)2(THF)4]n (1)

A single crystal X-ray structural analysis of complex (1) was carried out; a perspective view of the structure is shown in Fig. 1 and selected bond lengths and angles are presented in Table 1. [Cd3(TFA)4(OAc)2(THF)4]n is a one-dimensional coordination polymer, forming chains running parallel to the a axis. The structure contains two independent cadmium ions. Cd2 is six-coordinate and lies on the centre of symmetry, it is coordinated to one oxygen donor from each of the two independent triflate groups and one acetato anion. Inversion, under symmetry operation −x, −y, −z + 1, −z + 1 completes the approximately octahedral coordination sphere. Cd3 has less regular geometry and is seven-coordinate, bonded to one oxygen donor from each of two triflate groups and one acetato anion, a second bidentate acetate group and two THF molecules. The triflate anions each form 1,3-bridges linking Cd1 to Cd2 and these are also linked by the acetate group which forms a one-atom bridge (O31). Cd1 is linked to its symmetry equivalent under symmetry operation −x, −y + 1, −z + 1 via one-atom bridges formed by the second oxygen atom of the acetate ligand (O32). The coordination of the acetate group is unusual; it is a bidentate ligand to Cd1 and a monodentate ligand to Cd2 and a second Cd1 (under operation −x, −y + 1, −z + 1), both oxygen atoms are coordinated with both syn and anti-geometry. There are no notable interactions between the chains.
phase begins with the loss of two trifluoroacetate groups showing a weight loss of 34.9% of the total mass of the complex (1) at 328.7 °C. Most of the compound has been degraded before the onset of the final pyrolysis stage. The final step of the weight loss begins at 448 °C yielding a solid residue. Further heating of the residue to 600 °C did not bring any change in weight indicating complete decomposition of (1) to furnish a 34.2% of the residual mass, which is a little greater than the expected value of 32% for CdO as indicated in the chemical equation below:

\[
\text{[Cd}_4\text{(TFA)}_4\text{(OAc)}_2\text{(THF)}_4\text{]}_n \xrightarrow{450^\circ C} n\{3\text{CdO} + \text{volatiles}\}
\]

### 2.3 Powder X-ray diffraction studies

A representative powder X-ray diffraction pattern of zinc-cadmium oxide solid solution thin films prepared in THF solution is shown in Fig. 3. Similar patterns were observed for films deposited from methanol and ethanol and are given in the ESI (Fig. S7 and S8†). All the diffraction peaks can be indexed to the hexagonal wurtzite structure of ZnO with lattice constants of \( a = 3.25 \) and \( c = 5.22 \) Å, and the diffraction pattern matches well with the literature. In the XRD, peaks at 2θ values of 31.68°, 34.36°, 36.1°, 47.42° and 56.2° correspond respectively to (100), (002), (101), (102) and (110) lattice reflection planes of a hexagonal wurtzite structure showing that the 17% substitution of small Zn (\( r = 74 \) Å) by the large Cd (\( r = 97 \) Å) atoms did not bring any change in the original hexagonal structure of ZnO. Furthermore, no impurities such as CdO (intense peak at 2θ = 44.228°) or formation of any other phase were detected.

### 2.4 Surface morphology

The surface morphology of zinc-cadmium oxide alloy thin films grown on FTO coated glass substrates was investigated by field-emission scanning electron microscopy (FESEM). The films deposited from the common solutions of the precursors in three different solvents THF, methanol and ethanol at 500 °C for 45 min are presented in Fig. 4. The results illustrate that the morphology of the films changes significantly with the change of the deposition solvent. The film deposited using methanol as a solvent shows (Fig. 4a) particles of an average size of 0.2 μm that agglomerate to form large heaps. On the other hand, films deposited using ethanol as a solvent show a fine large spherical crystallite with an average size of 0.7 μm (Fig. 4b). Results of SEM of films fabricated from THF solution reveal the formation of needle-shaped particles with an average size of 70 nm. We believe that film formation by the AACVD process involves homogeneous and heterogeneous processes. The choice between homogeneous and heterogeneous reactions mostly depends on physical properties such as boiling point, density, surface tension and heat of combustion of the solvent. Solvents with low boiling point and higher heat of combustion yield thin films \( \text{via} \) a homogeneous process while solvents with high

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Table 1: Selected bond lengths [Å] and angles [°] from single crystal structure analysis of 1

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<th>Bond/Angle</th>
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<td>Cd1-O31</td>
<td>2.2926(17)</td>
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<td>Cd1-O32</td>
<td>2.788(2)</td>
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<td>Cd1-O41</td>
<td>2.2975(19)</td>
</tr>
<tr>
<td>Cd1-O51</td>
<td>2.3799(18)</td>
</tr>
<tr>
<td>Cd1-Cd2</td>
<td>3.9010(2)</td>
</tr>
</tbody>
</table>

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Fig. 2: TGA/DTG curves showing thermal decomposition of complex (1) to stable CdO residue.

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*a Symmetry transformations used to generate equivalent atoms: A: \( -x, -y+1, -z+1 \) and B: \( -x+1, -y+1, -z+1 \).
boiling and lower heat of combustion contribute to the heterogeneous process of film formation. We believe that in our case both the homogeneous and heterogeneous processes are involved in film formation with greater tendency of homogeneous reaction in THF.

EDX analysis of the thin films deposited at 500 °C in THF, methanol and ethanol as solvent indicate cadmium to zinc ratio as 0.17 : 0.83, 0.15 : 0.85 and 0.08 : 0.92 respectively, which is less than the atomic concentrations of cadmium to zinc in the depositing solution. The solubility of cadmium in the zinc oxide structure depends on the particle size of the material. The films formed in methanol agglomerate to form large heaps, whereas in ethanol solution round particles with an average diameter of 0.7 µm are found. The particle size of the film deposited from THF solution falls in the nanorange of 70 nm and the cadmium contents in these films are evaluated to be 17% which is larger than the films deposited from methanol and ethanol. The thermodynamic solubility of cadmium in the zinc oxide bulk material is small compared with that found for the nano-material. It has already been reported that the lattice in nano-structured zinc oxide becomes elastically soft that permits the dissolution of more cadmium atoms compared to the rigid bulk structure. Although the concentration of the precursors (I) and Zn(CH₃COO)₂·2H₂O was kept at 50% in all the three solutions (methanol, ethanol and THF), the high concentration of cadmium in films deposited from THF is a result of the dependence of the solubility of cadmium on the ZnO particle size.

2.5 Band gap
We have chosen thin films having particle sizes in the nanorange and possessing high concentrations of cadmium for band gap measurements. The optical absorption spectrum of thin films deposited at 500 °C using THF solvent having a thickness of 350 nm (profilometer KLA Tencore P-6 surface profiler) was recorded on a Lambda 35 Perkin-Elmer UV-visible spectrophotometer in the wavelength range of 300–850 nm using a similar FTO coated glass substrate as a reference to exclude the substrate contribution in the spectrum. The UV-visible spectrum of the Zn₀.₈₃Cd₀.₁₇O thin film shows an absorption edge at 402 nm and the band gap was calculated by plotting the Tauc plot of energy versus (αhν)² to give a value of 2.40 eV (Fig. 5) for the band gap. It is reported in the literature that band gap of Zn(1₋ₓ)CdₓO solid solution thin films highly depends on the value of x (cadmium contents), which shows the band gap of 2.3 and 2.5 eV for 20 and 14% Cd contents respectively. In our case incorporation of 17% Cd gave a band gap of 2.4 eV that is in a good agreement with the reported value.

2.6 Photoelectrochemical properties of Zn₀.₈₃Cd₀.₁₇O thin films
The effect of nature of solvent, film deposition temperature and electrolyte concentration on photoresponse of the thin film electrodes under illumination (L) and dark (D) conditions was investigated and presented in Fig. 6. It is evident that
photocurrent density heavily depends on morphology, deposition temperature and electrolytic concentration. The photoelectrodes deposited from THF solution at 500 °C produce the maximum photocurrent in 0.5 M NaOH solution. The formation of nanorod shaped structures from THF deposition solution is attributed to the higher heat of combustion of THF (2501 kJ mol\(^{-1}\)) as compared to methanol (736 kJ mol\(^{-1}\)) and ethanol (1370 kJ mol\(^{-1}\)).

The photocurrent density increases with the increase in deposition temperature and reaches a maximum at 500 °C (Fig. 6b). With further increase of the deposition temperature, the photocurrent of Zn\(_{0.83}\)Cd\(_{0.17}\)O photoelectrodes decreases significantly. We believe that at the low substrate temperature regime, the decomposition was not completed and as a result the nanocrystals became rich in defects, leaving dislocations and kink sites. These dislocations and kink sites may act as recombination centres for the photogenerated electron–hole pairs and consequently show a poor PEC performance. Similarly, at a higher temperature regime (>500 °C) premature decomposition and nucleation influence the film morphology and texture diminishing the photocurrent. It is reported for the AACVD technique that at higher temperatures, the decomposition of the precursor starts much earlier in the gas phase and homogeneous nucleation produces powdered particles before depositing on the substrate surface and resulting films have more defects and possess less adherence properties.

Besides the deposition solvents and temperature, the effect of concentration of the electrolyte was also found to be an important factor in determination of photocurrent density. Thin films synthesized from THF at 500 °C give different photocurrent responses on changing the electrolyte (NaOH) concentration (0.1, 0.5, 1 and 2 M). Fig. 6c shows the highest response for the Zn\(_{0.83}\)Cd\(_{0.17}\)O thin films studied at 0.5 M NaOH. It is true that at low concentration (0.1 M) the interaction between the fabricated layer and the electrolyte is less, thus the photocurrent density becomes low. Whereas, in higher concentrations (1 and 2 M), strong interaction between the electrolyte and the thin film surface leads to high mass transfer and poor photocurrent response.

**2.6.1 Electrochemical Impedance Spectroscopic (EIS) studies.** The linear sweep voltammetry (LSV) results were further buttressed by EIS studies. Fig. 7 shows that the diameter of semi-circles in the Nyquist plots change with the change of charge transfer resistance due to the different photo-electrochemical properties of the layers. From the comparison of simulation and experimental data of the fabricated layers in the presence and absence of light, the most accurate equivalent circuit model for all the semicircles is \(R_s([C]R_{Q_p}(R_{Q_c}Q))\).

Instead of the pure capacitance (C), a constant phase element (CPE, written as \(Q\) in the circuit model) is introduced in the simulation process to obtain a good agreement between simulated and experimental data. The impedance (Z) of the CPE is defined as \(Z_{CPE} = [Q(i\omega)^n]^{-1}\), where \(Q\) (\(\Omega^{-1}\) s\(^{-n}\) cm\(^{-2}\)) is the combination of properties related to both the surface and the electroactive species independent of frequency.\(^{21}\) The “n” value also depends on the surface homogeneity. The obtained parameters from equivalent circuits are tabulated in Table 2.
be manifested that the ethanol and THF respectively thin layers with light (150 W). Consequently, a good agreement between EIS and interface of electrolyte into the pores. However, Table 2 gives parameters such as capacitance which occurs with the charge transfer process. Table 2 shows lower charge transfer resistance in the presence of these photo-electrochemical parameters can be explained as follows. $R_s$ is the solution resistance between the WE and RE, $R_{po}$ is the pore resistance which is due to the formation of pores in the layers. $C_{po}$ is the capacitance of the pores, from the interface of electrolyte into the pores. However, $R_{po}$ and $C_{po}$ form a parallel combination. The second parallel combination is due to the charge transfer resistance ($R_{ct}$) and CPE, which is in series with $R_{po}$. The CPE is often approximated to the double layer capacitance which occurs with the charge transfer process. Table 2 gives parameters such as $C_{po}$, $R_{po}$, $R_{ct}$, and CPE values. It can be manifested that the $R_{ct}$ value of the Zn$_{1-x}$Cd$_x$O layers deposited in THF is much smaller than the other two fabricated layers (in ethanol and methanol) in the absence and presence of light (150 W). Consequently, a good agreement between EIS and LSV results was found. The same procedure was done for the Zn$_{1-x}$Cd$_x$O layers with different concentrations of NaOH (Fig. 7c) and at different temperatures (Fig. 7b). Fig. 7c shows that the diameter of the semicircle in the Nyquist plot becomes larger due to the low interaction between the Zn$_{0.83}$Cd$_{0.17}$O layer and the electrolyte (0.1 M). This is due to the higher charge transfer resistance ($R_{ct}$) value. It can be seen that the charge transfer resistance for the Zn$_{0.83}$Cd$_{0.17}$O layer is also high at higher concentrations of NaOH (2 M). This phenomenon could be due to the surface passivation of the deposited layer at higher concentration of NaOH (2 M), which inhibits the charge transfer process across the electrode–electrolyte interface, resulting in a higher charge transfer resistance ($R_{ct}$) value. The formation of passive ZnO and Zn(OH)$_2$ layers on the surface of Zn is known to occur in high concentrations of alkaline solutions, thus inhibiting the charge transfer process. Nevertheless the results in Table 2 show lower charge transfer resistance in the presence of light compared to its absence, due to the reasonable interaction between the Zn$_{0.83}$Cd$_{0.17}$O layer and the electrolyte. Light irradiation induces a charge transfer process across the electrode–electrolyte interface, thereby lowering the charge transfer resistance ($R_{ct}$). It was found that the best photo-electrochemical behaviour was obtained in 0.5 M NaOH.

### Table 2

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<th>$R_s$ (ohm)</th>
<th>$R_{po}$ (ohm)</th>
<th>$C_{po}$ (F)</th>
<th>$R_{ct}$ (kohm)</th>
<th>CPE ($\Omega^{-1} \text{s}^n$)</th>
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2.6.2 Minimum responsivity measurements. The minimum responsivity of thin films to the light radiation was observed by eqn (1) at 0.5 V.

$$\text{Minimum responsivity} = \frac{(I_{\text{illuminated}} - I_{\text{dark}})}{W_{\text{max}}}$$  (1)
3 Experimental section

3.1 Materials and methods

All manipulations were carried out under an inert atmosphere of dry argon, using Schlenk tubes and glove box techniques. The solvents and reagents were purchased from Aldrich. The solvents were rigorously dried on sodium benzphenoate and distilled immediately before use. The melting point was determined in a capillary tube using an electrothermal melting point apparatus; model MP-D Mitamura Riken Kogyo (Japan). The microanalyses were performed using Leco CHNS 932. FT-IR spectra were recorded on a single reflectance ATR instrument (4000–400 cm⁻¹, resolution 4 cm⁻¹). The NMR was recorded using a JEOL DELTA2 NMR spectrometer at a field strength of 400 MHz using deuterated DMSO as a solvent. The controlled thermal analysis was investigated using a METTLER TOLEDO TGA/SDTA 851e Thermogravimetric Analyzer with a computer interface. The thermal measurements were performed in an alumina crucible under an atmosphere of flowing nitrogen gas (50 cm³ min⁻¹) with a heating rate of 20 °C min⁻¹.

3.2 Synthesis of [Cd₃(TFA)₄(OAc)₂(THF)₄]ₙ (1)

A mixture of cadmium(II) acetate dihydrate (1.0 g, 3.7 mmol) and trifluoroacetic acid (0.375 mL, 4.93 mmol) in 30 mL of THF in a Schlenk tube under argon atmosphere was stirred for 8 h. The reaction mixture was filtered to remove any unreacted material. The filtrate was concentrated under vacuum and complex (1) was isolated from THF solution in 80% yield. Mp: 85 °C. Microanalysis: % calcd (found) for [Cd₃(TFA)₄(OAc)₂(THF)₄]ₙ C, 28.11 (28.12), H, 3.1 (2.8). FT-IR/ cm⁻¹: 1679 s, 1552 s, 1442 w, 1415 s, 1193 s, 1138 s, 1035 w, 836 w, 794 s, 720 ms. ¹H NMR (DMSO) δ = 3.60 ppm [s, 16H, OCH₃(THF)₄]; δ = 1.85 ppm [s, 6H, CH₃(OAc)]; δ = 1.76 ppm [p, 16H, CH₂(THF)]. ¹⁹F NMR (DMSO) δ = −73.60 ppm [s, 12F, CF₃]. TGA: 107.7 °C 5.8%; 107.7–278.5 °C 35.5%; 328.7 °C 54.9 and 448 °C 65.8% weight loss. Crystals suitable for single crystal X-ray diffraction study were obtained from THF.

Crystal data for 1: C₃₀H₃₈Cd₃F₁₂O₁₆, Mᵣ = 1195.78, triclinic, a = 9.5553(4) Å, b = 9.6390(5) Å, c = 12.4046(6) Å, α = 69.4820(10)°, β = 70.6980(10)°, γ = 87.2930(10)°, V = 1006.83(8) Å³, space group Pt, Z = 1, μ = 1.691 mm⁻¹, 13 937 reflections measured, 5001 independent reflections (Re = 0.0181). Final R₁ and wR₂ values were 0.0266 and 0.0692 for I > 2σ(I) and 0.0304 and 0.0704 for all data; goodness of fit on F² was 1.054.

The data were collected at 150(2) K on a Bruker Apex II CCD diffractometer using MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SIR-2004) and refined on F² using all the reflections (SHELX). All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions using a riding model.

3.3 Deposition of thin films by AACVD

The thin films were deposited on a commercially available FTO glass substrate using locally-designed Aerosol Assisted Chemical Vapour Deposition assembly. The substrates were cleaned prior to use by ultrasonically washing with distilled water, acetone, and then ethyl alcohol. Finally, they were washed with distilled water, stored in ethanol, and dried in air. In a typical deposition, Zn(CH₃COO)₂·2H₂O (0.153 g, 0.69 mmol) and [Cd₃(TFA)₄(OAc)₂(THF)₄]ₙ (0.833 g, 0.69 mmol) were dissolved in a 50 mL round bottom flask using common solvents to make a homogeneous solution from which thin films of Zn(1–x)CdₓO formed using a deposition time of 45 minutes. Carrier gas at a flow rate of 120 mL min⁻¹ (controlled by a L1X linear flow meter) was used. Substrate slides (1 cm × 2 cm) were placed inside the reactor tube and then heated up to the deposition temperature of 500 °C for 10 min before carrying out the deposition. The aerosols of the precursor solution were formed by keeping the round bottom flask in a water bath above the piezoelectric modulator of an ultrasonic humidifier. The generated aerosol droplets of the precursor were transferred into the hot wall zone of the reactor by carrier gas. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. At the end of the deposition the aerosol line was closed and only carrier gas was passed over the substrate. The substrate was allowed to cool to 30 °C before it was taken out from the reactor. The films of different morphology, thickness and nanostructure were deposited in three different solvents (THF, methanol and ethanol) and at three different temperatures (475, 500 and 525 °C). The deposited thin films are light yellow in colour, transparent, uniform, robust, and stable towards atmospheric conditions and adhere strongly onto the FTO substrate as verified by the “scotch tape test”. The elemental ratio determined by EDX of thin films in THF, methanol and ethanol as solvent showed cadmium to zinc ratios as 0.17 : 0.83, 0.15 : 0.85 and 0.08 : 0.92 respectively.

3.3.1 Characterization of thin films. The surface morphology of thin films was studied using a field-emission
gun scanning electron microscope (FESEM, FEI Quanta 400) coupled with an Energy Dispersive X-ray spectrometer EDX (INCA Energy 200 (Oxford Inst.)), at an accelerating voltage of 10 kV, and a working distance of 6 mm.

The final products were characterized using X-ray powder diffraction (XRD) on a D8 Advance X-Ray Diffractometer-Brucker AXS using Cu-Kα radiation (λ = 1.504 Å), at a voltage of 40 kV and a current of 40 mA at ambient temperature. The optical absorption spectrum of the thin films deposited at 500 °C using THF solvent having a thickness of 350 nm (profilometer KLA Tencore P-6 surface profiler) was recorded on a Lambda 35 Perkin-Elmer UV-visible spectrophotometer in the wavelength range of 300–850 nm. The photo-electrochemical response of fabricated Zn0.8Cd0.15O layers was studied by electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and linear scanning voltammetry (LSV) in the presence and absence of sunlight (150 W). A three-compartment cell with a saturated calomel electrode (SCE) as the reference electrode (RE) and Zn0.8Cd0.15O/FTO (0.5 × 1 × 1 cm) as the working electrode and Pt wire as a counter electrode was used for the photocurrent measurements. Frequency response analysis (FRA) software was used in the EIS experimental and simulation experiments while general purpose electrochemical software (GPES) was used in the linear scan voltammetry (LSV) using an Autolab PGSTAT-302N. The scan rate for LSV was 10 mV s⁻¹ between −0.3 V and 0.6 V while the EIS measurements were carried out at a frequency range of 100 kHz to 10 mHz.

4 Conclusion

In summary hexagonal nanostructured zinc-cadmium oxide solid solution Zn₁₋ₓCdₓO thin films were deposited on FTO coated glass substrates from a common solution of zinc acetate and a newly developed polymeric cadmium precursor [Cdₓ(TFA)₃(OAc)₃][THF]₃]ₓ (1) by the aerosol-assisted chemical vapour deposition (AACVD) technique and applied for photo-electrochemical water splitting. Various parameters have been studied to optimize the conditions for fabrication of stable, robust and efficient photoelectrode thin films. The SEM analysis of the photoelectrode thin films shows that the morphology of the grown thin films strongly depends upon physical characteristics of the solvent. Photoelectrodes grown out of THF solution have higher concentration of Cd and showed to have better photocatalytic activity than the photoelectrodes grown from methanol and ethanol that have lower Cd concentration. A band gap of 2.40 eV and a photocurrent density of 0.23 mA cm⁻² at 0.60 V vs. Ag/AgCl/3 M KCl (~1.23 V vs. RHE) have been obtained for photoelectrodes grown from THF solution that indicates that the material has potential for photoelectrochemical and solar energy applications such as photovoltaic cells and photocatalytic decomposition of organic contaminants.

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References


