Chemically Vaporized Cobalt Incorporated Wurtzite as Photoanodes for Efficient Photoelectrochemical Water Splitting

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Abstract

The development of low-cost, durable and efficient photocatalyst for overall photoelectrochemical water splitting is in demand to overcome the renewable energy crises. Herein, we demonstrate the efficient photoelectrochemical water splitting by cobalt (Co) incorporated zinc oxide (Zn$_{1-x}$Co$_x$O) thin films deposited via aerosol assisted chemical vapour deposition (AACVD) technique. The as-deposited Co incorporated ZnO thin films were characterized by powdered X-ray diffraction (pXRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and ultra violet-visible spectroscopy (UV-Vis). These films with different concentration of cobalt were investigated for water splitting applications and the best results were achieved for the films with 15% Co incorporation.

**Key words:** ZnO, thin films, AACVD, water splitting, PEC.
**Introduction**

Recently, research in photoelectrochemical (PEC) water splitting has gained enormous attention to overwhelm the global energy crises.\(^1\)-\(^4\) In this context, various photoanodic materials including GaS, GaP, CdSe, CdS, Fe\(_2\)O\(_3\), TiO\(_2\), ZnO, WO\(_3\), SnO\(_2\) and SiC have been tested for PEC systems.\(^5\)-\(^9\) Among aforementioned materials, thin films and nanostructured of TiO\(_2\) have been extensively studied for PEC water splitting applications due to its ideal band gap (~3.2 eV) alignment with redox potential of water and superior photo-thermal stability.\(^10\)-\(^12\) However, it has some intrinsic limitations such as fast charge carriers recombination and low absorption coefficient in visible region of electromagnetic spectrum.\(^13\),\(^14\) Moreover, phase controlled synthesis due to existence of polymorphism and high annealing (~ 500 °C) temperature for the desired photoactive crystalline phase are another major challenges associated with this material.\(^15\)

On the other hand, ZnO have band gap energy similar to TiO\(_2\), has emerging as low cost, direct band gap material, which is non-toxic, greener oxide with high electron mobility and good photo-stability.\(^16\)-\(^18\) Furthermore, zinc oxide (ZnO) has structural diversity and exists in three crystalline forms; hexagonal wurtzite, cubic zinc blende and cubic rocksalt. Among these phases, wurtzite has highest thermodynamic stability with superior electronic properties.\(^19\),\(^20\) Owing to these properties, ZnO has been widely explored for PEC water splitting applications, however, the wide band gap (3.3 eV) is the major limitation, which hampered its potentiality towards PEC water splitting application. To modify the structural and electronic structures of wide band gap semiconductors, metal ions incorporation have appeared to be an effective strategy.\(^21\)-\(^24\) Apart from this, the use of solution processed ZnO nano-materials for PEC applications have also been used.\(^23\),\(^25\),\(^26\) However, ZnO nanomaterials were found reactive to undergo considerable segregation that results in difficulty of synthesis and handling of desired electrodes in different pH media. To overcome this issue, one of the possible way is to use ZnO thin films (~ 1-100 nm thickness) to prepare electrode.\(^27\),\(^28\)
ZnO thin films can be fabricated by various techniques including, magnetron sputtering, pulsed laser deposition, molecular beam epitaxy, chemical vapor deposition, ultrasonic spray pyrolysis, hydrothermal and resonance frequency (RF) and direct current (DC) plasma jet sputtering systems have been employed. However, chemical vapour deposition (CVD) approach has received considerable interest in recent years to prepare thin films of metal-chalcogenide and metal oxide materials. Aerosol assisted chemical vapours deposition (AACVD) is a modified form of CVD which can efficiently produce thin films on various substrates. The films obtained via this technique has numerous advantages as it does not need annealing or calcination separately. Thus, AACVD offers smart way to prepare high quality, uniform thin films in short-time.

In present work, Pristine ZnO and Co incorporated ZnO thin films were deposited on FTO substrates via aerosol assisted chemical vapour deposition technique at 400°C. The as-deposited thin films have been characterised by using wide range of characterization techniques. The Co incorporation in ZnO to form impurity levels that expands the optical absorbance to visible range. Therefore, Co incorporated ZnO thin films have shown promising PEC water splitting performance under visible light. The as-deposited electrode showed excellent stability under applied condition.

**Experimental Section:**

**Materials**

Zinc acetate dihydrate, (99.9 %, Sigma Co.), cobalt acetate tetrahydrate, (99.9 % Sigma Co.) and methanol (99.9 % Sigma Co.) were used as received, without further purification.

**Characterizations**

The crystal structures of ZnO and Co-doped ZnO thin films were studied by D8 ADVANCE XRD (Bruker, Germany) using Cu.Kα radiation ($\lambda = 1.54178 \text{ Å}$), in a 2θ range from 15° to 80°. FESEM TESCAN MIRA3XMU Scanning Electron Microscope (SEM) along
with EDX (JEOL, USA) was used for the study of structural morphology of the thin films. The size of particles and structural confirmation was evaluated by Transmission Electron Microscopy (TEM) and high resolution transmission electron microscope (HRTEM) using Ion Company (FEI) Tecnai G2 F20 S-Twin microscope at 200 kV. The reflectance of the thin films was measured by SHIMADZU UV 1800 Spectrophotometer.

All electrochemical measurements were carried out using an Auto lab PGSTAT12 potentiostat. In three-electrode measurements, 1 M Na$_2$SO$_4$ was used as an electrolyte with Co-ZnO/FTO as working electrode, a Pt wire as a counter electrode and Ag/AgCl reference electrode in a 5 mL quartz cell.\textsuperscript{37} For all cyclic voltammetry experiments, two scans were obtained, only the second scan is presented in the data. These measurements were carried out at various scan rates between the voltage window of 0 and 1 V. The stability was measured by using the time period of about half an hour.

**Fabrication of Zn$_{1-x}$Co$_x$O solid solution photoanodes**

Thin films of pristine and cobalt incorporated ZnO were on glass substrates by means of a home-built aerosol assisted chemical vapour deposition (AACVD) technique reported elsewhere.\textsuperscript{38,39} Prior to deposition, the substrates were cleaned ultrasonically with a mixture of 2.5 mL of hydrochloric acid (12 M) and 2.5 mL of deionized water for 20 minutes and finally rinsed with 5 mL of acetone. For deposition of pristine ZnO thin films, 0.8 g (4 mmol) of zinc acetate dihydrate was dissolved in 20 mL methanol, while for Co incorporated ZnO thin films, 0.8 g (4 mmol) of Zinc acetate dihydrate was mixed with calculated amounts of cobalt acetate tetrahydrate (0.08, 0.2, 0.4 and 0.6 mmol) in 20 mL of methanol to produce 2%, 5%, 10% and 15% Co incorporated ZnO thin films. The corresponding precursor solution was stirred for 30 minutes, transferred to a two-necked round bottom flask and placed in water bath above the piezoelectric modulator of an ultrasonic humidifier to generate aerosols. The generated
aerosols were carried to the horizontal tube furnace (Carbolite furnace) by using Argon as carrier gas at the flow rate of 200 sccm, where six glass slides were placed and temperature of tube furnace was maintained at 400 °C. The deposition in all cases were performed for 2 hours. Same procedure and conditions were adopted to deposit Co incorporation ZnO thin films on FTO substrate and used for photoelectrochemical measurements.

Results and discussion

The thin films of pristine ZnO and Co incorporated ZnO were fabricated by aerosol assisted chemical vapour deposition (AACVD) method at 400 °C. The Co incorporation in ZnO leads to gradual change in colour of thin film from pale yellow (pristine ZnO) to green (light green for 2% and 5% Co incorporation and dark green for 10 % and 15 % Co incorporation). The visual change in colour of as-deposited thin films indicates the successful incorporation of cobalt in ZnO lattice. Powdered XRD was used to determine the crystal structure of pristine ZnO thin film and cobalt incorporated ZnO thin films as shown in (figure 1a). The diffraction peaks of all as-deposited thin films located at 2θ (°) ~ 31.82, 34.33, 36.49 and 47.56, which corresponds to (100), (002), (101) and (102) planes of hexagonal wurtzite ZnO structure (ICPDS No. 086254). The relative peak intensities of various planes were unaffected upto to 5% Co incorporated ZnO, however, there is a gradual decrease in relative peak intensities with the increased incorporation of cobalt contents (10%, 15%). Furthermore, the peak positions were shifted to higher angles (0.1°) in all diffraction peaks of 15% cobalt incorporation in ZnO as shown in figure 1b. This shift in diffraction peaks is due to the smaller ionic radius of tetrahedral coordinated Co\(^{2+}\) ion (0.58 Å) as compared to Zn\(^{2+}\) (0.60 Å).\(^{40,41}\) The absence of extra peaks in ZnO and Zn\(_{1-x}\)Co\(_x\)O thin films confirms the phase pure crystalline structures. The p-XRD spectra of as –deposited thin films suggest that the Co ions have been substituted in the ZnO lattice\(^{42}\).
Surface morphology of as-deposited Zn_{x-1}Co_xO (x = 0.02, 0.5, 0.1, 0.15) thin films was determined by field emission scanning electron microscopy (FE-SEM). Figure 2(a-c) represents the micrographs of Zn_{1-x}Co_xO (x = 0.02, 0.5, 0.1, 0.15) thin films. The thin film deposition was found smooth and uniform in all deposited samples. However, significant differences in morphologies were observed upon cobalt incorporation in ZnO thin films. Figure 2a shows typical morphology of as-deposited pristine ZnO thin films by AACVD at 400 ºC. The crystallites have mixed morphology (circular, oblong) with average size 1.50 ± 3 μm. Similarly, figure 2b shows the elongated structures of Zn_{0.98}Co_{0.02}O thin films with average size 1.8 ± 2μm. With the rise of contents of cobalt from 2% to 5%, larger size of crystallites with well-defined boundaries were obtained (figure 2c). However, further increase in Co concentration (10%) to get Zn_{0.90}Co_{0.1}O produces thin films of reduced sized elongated grains.
172 (figure 2d). 15% Co incorporation in ZnO forms the hierarchal interlinked structures. The
173 formation of hierarchal structures in Zn$_{0.85}$Co$_{0.15}$O film suggests that these films could allow
174 fast electron transfer.

Figure-2: FESEM images of (a) pristine ZnO (b) 2% Co in ZnO, (c) 5% co in ZnO, (d)
10% co in ZnO and (e-f) 15% Co in ZnO thin films at different magnifications.

To confirm the presence of Co in ZnO thin films, the elemental mapping was performed to
176 confirm the distribution of elements in as-deposited thin films using energy dispersive X-ray
177 spectroscopy (EDX). Figure S1 (a-d); (supporting information) shows distribution of Zn, Co
178 and O in the interrogated area of as-deposited thin films.

Figure 3(a-b); shows TEM and HRTEM images of 15% Co incorporated in ZnO thin
179 film. It can be observed that the formation of network of knotted crystallites of average size ~
180 30 ± 4 nm as shown in (figure 3a). The lattice fringes of 15% Co incorporated ZnO was
181 estimated to be 2.2 Å, which corresponds to the (101) plane of wurtzite ZnO.
Further surface topography and structural analysis of as-deposited cobalt incorporated ZnO thin films were performed by atomic force microscope (AFM) as shown in Figure 4.

**Figure-3:** (a) Transmission electron microscope (TEM) image of as-deposited 15% Co incorporated ZnO thin films by AACVD, (b) high resolution TEM image with vivid lattice fringes, Inset represents corresponding EFT image.

**Figure-4:** AFM images of (a, b) ZnO (c, d) 10% Co-ZnO thin films
The optical properties of ZnO, and Co incorporated ZnO thin films were determined by UV-Visible diffuse reflectance spectroscopy (UV/DRS) at room temperature. Figure 5a shows that the band edge absorption of pristine ZnO thin film was appeared at 372 nm with maximum reflectance. However, the Co incorporation in ZnO expands the optical absorbance in visible region. In Co incorporated ZnO ($x = 0.02, 0.5, 0.1, 0.15$) three new absorption peaks were observed at 569 nm, 617 nm and 660 nm. Moreover, with the increase in Co impurity level in ZnO, the optical absorption intensity was increases monotonically with corresponding decrease in reflectance. The appearance of new absorption peaks in Co incorporated ZnO samples was due to the sp-d exchange interactions between the band electrons and the localized d electrons of incorporated Co.\(^{43}\)

![Figure 5](image.png)

**Figure 5:** (a) Diffused reflectance spectra, (b) Kubelka-Munk plots for band gap energy and (c) band gap vs thin film composition of pristine and Co incorporated ZnO (2%, 5%, 10% and 15%) solid solution thin films.

Kubelka-Munk treatment has been applied to determine the band gap energy of as-deposited Zn\(_{1-x}\)Co\(_x\)O ($x = 0.02, 0.5, 0.1, 0.15$) ZnO solid solution thin films as shown in (figure 5b). The band gap of pristine ZnO films was found to be 3.25 eV. The decrease in band gap
was observed by increasing impurity level of Co in ZnO. The observed band gaps were 2.75 eV, 2.7 eV, 2.58 eV and 2.54 eV for 2%, 5%, 10% and 15% Co incorporation, respectively. The observed decrease in band gap energy with Co incorporation is well matched with previous literature reports\textsuperscript{43}. This red shift in band gap is probably due to the overlapping of ZnO conduction bands with 3d electrons of Co\textsuperscript{2+} ions \textsuperscript{44}. The decrease in band gap was also supported by observed change in colour of as-deposited thin films as shown in (figure 5c).

Photoelectrochemical (PEC) studies were carried out by using three-electrode system with 1M Na\textsubscript{2}SO\textsubscript{4} as an electrolyte. The electrochemical surface area (ECSA) was measured for all as-deposited electrodes using cyclic voltammetry (CV) in 1 M Na\textsubscript{2}SO\textsubscript{4} solution with three-electrode system (Zn\textsubscript{1-x}Co\textsubscript{x}O/FTO as working electrode, Pt wire acts as a counter electrode, and Ag/AgCl as reference electrode) at different scan rates ranging from 0.1-0.5 V/s via double layer capacitance. The corresponding CV curves for as-deposited electrode are presented in figure S2 (a-d); (supporting information). Figure 6\textsuperscript{4} shows the charging current density differences for all as-deposited thin films. The slope of graph gave double layer capacitance (cdl) of as-deposited Zn\textsubscript{0.98}Co\textsubscript{0.02}O, Zn\textsubscript{0.98}Co\textsubscript{0.02}O, Zn\textsubscript{0.98}Co\textsubscript{0.02}O, and Zn\textsubscript{0.98}Co\textsubscript{0.02}O films, which were found to be 0.42 mF/cm\textsuperscript{2}, 0.45 mF/cm\textsuperscript{2}, 0.53 mF/cm\textsuperscript{2} and 0.64 mF/cm\textsuperscript{2} respectively. The Zn\textsubscript{0.85}Co\textsubscript{0.15}O thin films have shown higher cdl value compared to Zn\textsubscript{0.98}Co\textsubscript{0.02}O, Zn\textsubscript{0.95}Co\textsubscript{0.05}O and Zn\textsubscript{0.90}Co\textsubscript{0.10}O due to enhanced active surface area and diffused morphologies, which results in superior charge storage. These results suggest that Zn\textsubscript{0.85}Co\textsubscript{0.15}O thin films could show better photoelectrochemical results.
The photoelectrochemical water splitting performance of pristine ZnO and Co incorporated ZnO at different concentrations under light and dark conditions are shown in the (figure 7a). Under dark conditions, the as-deposited photoanodes have shown negligible current generation at applied potential shown in (figure S3). However, under irradiation of solar light AM 1.5 with typical intensity 100 mW/cm², the increase in photocurrent density was observed. Pristine ZnO thin films show photocurrent density of about $1.296 \times 10^{-4}$ Acm⁻², which is quite low due to large band gap of ZnO (3.2 eV) and un-diffused grain boundaries as observed in the (figure 5a). However, 2% Co incorporation in ZnO results in the 46% increase in current density ($2.81 \times 10^{-4}$ Acm⁻²) due to increase in band gap of as-deposited photoanode (Zn₀.₉₈Co₀.₀₂O). Further, 5%, 10% and 15% Co incorporation in ZnO (photoanodes) leads to increase in current density from $2.81 \times 10^{-4}$ to $9.27 \times 10^{-4}$ Acm⁻² at 0.7 V versus RHE. The highest photoelectrochemical water splitting response of Zn₀.₈₅Co₀.₁₅O is directly related to the electrode morphology, which becomes more complex and diffused compared to ZnO making it suitable for the better charge transportation. Moreover, the smaller band gap of Zn₀.₈₅Co₀.₁₅O results in deceasing the electron hole pairs recombination rate and enhance the charge transport properties of as-deposited photoanode.⁴⁵ Furthermore, the PEC performance under dark and
light cycles was also confirmed. The linear sweep voltammetry (LSV) curves of ZnO and Zn$_{1-x}$Co$_x$O ($x = 0.02, 0.05, 0.1, 0.15$) thin films under chopped light illumination are represented in figure 7b. All the photo anodes show great photo-switching property with fast response. Among as-deposited photoanodes, the Zn$_{0.85}$Co$_{0.15}$O shows the highest light harvesting response value over the applied voltage range, due to slower recombination of electron hole pairs and efficient energy transfer mechanism of Co incorporated ZnO as compared to pristine ZnO thin films.  

![Figure 7: (a) Linear Sweep Voltammetry (LSV) Curve/Photocurrent-potential curve in light and dark (b) Chopped photocurrent-potential curve LSV for ZnO and Zn$_{1-x}$Co$_x$O thin films](image-url)

The photoelectrochemical kinetics of as-deposited photoanodes (ZnO, Zn$_{0.98}$Co$_{0.02}$O, Zn$_{0.95}$Co$_{0.05}$O, Zn$_{0.90}$Co$_{0.1}$O and Zn$_{0.85}$Co$_{0.15}$O) was calculated by Tafel plot as shown in figure 8. The values of Tafel slope for ZnO thin films was found to be 0.81 V. However, incorporation of Co in ZnO lattice decreases the Tafel slope values from 0.67, 0.56, 0.528, and 0.521 for the photoanodes at different concentrations (2%, 5%, 10% and 15%), respectively. A decrease in
Tafel slope values correlates to rapid catalytic reaction, thereby, facilitates the PEC activity.\textsuperscript{47}

![Tafel plots for as-deposited ZnO and Zn\textsubscript{1-x}Co\textsubscript{x}O thin films by AACVD](image)

**Figure-8:** Tafel plots for as-deposited ZnO and Zn\textsubscript{1-x}Co\textsubscript{x}O thin films by AACVD

The **photo stability** of photoanode for photoelectrochemical water splitting is an important parameter. The photocurrent stability was assessed for all as-deposited photoanodes under repeated illumination-darkens cycle. The duration of each cycle was 10 seconds. Figure 9 shows that the photocurrent of as-deposited photoanodes was increased in the first cycle, afterwards, it decreases in second cycle and become constant onwards. The chronoamperometric measurements of Zn\textsubscript{0.85}Co\textsubscript{0.15}O showed high photo-stability. The photocurrent spike observed under irradiation may be due to capacitive charging of the interface, but with passage of time the current density stared to get stabilized with the disappearance of photocurrent spike,\textsuperscript{48,49} which may be due to the recombination of the charge carriers associated with holes getting trapped at the surface.\textsuperscript{50}
Conclusion

In conclusion, we reported the cobalt incorporated zinc oxide thin films (2%, 5%, 10% and 15%) fabricated by aerosol assisted chemical vapour deposition (AACVD) technique using zinc acetate dihydrate and cobalt acetate tetrahydrate as precursors at 400 °C for 2 hours. The cobalt incorporation in ZnO has expanded the absorption spectrum of ZnO to visible region, which results in enhancement of PEC performance of ZnO. Among aforementioned samples, the as-deposited Zn_{0.85}Co_{0.15}O have shown excellent photocurrent density of about $9.27 \times 10^{-4}$ A/cm$^2$ at 0.7 V versus RHE, with double layer capacitance at 0.64 mF/cm$^2$. These results suggest that Co incorporation in ZnO has improved the PEC performance of ZnO due to the expansion of absorption range and excellent charge transport and separation efficiency. This work will open a new opportunity to develop efficient heterostructural photoelectrodes for solar energy driven water splitting application.

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