Photochemical Deposition of Co-Ac Catalyst on ZnO Nanorods for Solar Water Oxidation

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The preparation of ZnO nanorod films decorated with cobalt-acetate (CoAc) electrocatalyst and its activity for photoelectrolysis of water have been demonstrated. The photochemically prepared CoAc catalyst is chemically and morphologically similar to the electrochemically prepared CoAc catalyst. The on-set potential of oxygen evolution reaction is lower on CoAc-ZnO photoanode in relation to bare ZnO photoanode. There is a three to four fold increase in photooxidation current of OER due to the presence of CoAc co-catalyst on ZnO. Thus, the photochemically prepared CoAc on ZnO is an alternative and efficient co-catalyst for photoelectrochemical oxygen evolution reaction. The enhancement in photocatalytic activity of ZnO by the CoAc catalyst photochemically deposited from acetate buffer solution is significantly greater than the cobalt-phosphate (CoPi) co-catalyst deposited from phosphate buffer solution.

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Hydrogen is a convenient fuel for the future owing to its high energy density and eco-friendliness.1,2 Currently, around 48 million metric tons of H2 is produced globally each year mainly from natural gas by steam-methane reforming method.3,4 As this process leads to the emission of a large amount of CO2 (240 mega tons per year), it is challenging to develop alternate, clean methods to produce hydrogen. Generation of hydrogen gas from water requires energy of 273 kJ mol−1. If this energy is available from a renewable energy source such as solar energy, hydrogen can be considered as an economical and green energy source, which is an alternative to fossil fuels.

A simple approach is to use photovoltaic cells to power water electrolyzers. However, diurnal variation in the sunlight intensity, a high cost and a low conversion efficiency impede successful commercialization of the present photovoltaic cells.5 Another approach is to store solar energy directly in the chemical bonds of small molecules, similar to the photosynthesis route adopted by vegetation. A typical example is the photodissociation of water to generate hydrogen fuel.6 The first report on photodissociation of water into H2 and O2 using n-type TiO2 photoanode and Pt black cathode was reported by Fujishima and Honda7 in 1972. Following this report, numerous investigations have been reported for photocatalytic and photoelectrochemical water splitting.8 Most of the studies suffer from poor solar to hydrogen conversion efficiency due to fast recombination of photogenerated charge carriers and poor catalytic activity of semiconductor electrodes toward multi-electron oxygen evolution reaction (OER) at the photoanode.9,10 Several metal oxides such as RuO2,11 IrO2,12,13 etc., are coupled with semiconductors (TiO2, ZnO, etc.) as co-catalysts to enhance the sluggish kinetics of water oxidation. However, high cost of Ru and Ir limit their widespread application. Recently, a cobalt-phosphate complex (CoPi) has been reported14 as an inexpensive and efficient catalyst. It has been reported that photoelectrochemical water oxidation is significantly enhanced when the CoPi is interfaced with semiconductor photoanodes such as Si,15 TiO2,16 BiVO4,17,18 WO319 etc., and its activity as a co-catalyst in photoelectrochemical (PEC) OER. Photochemical deposition is preferred to electrodeposition as it does not require any voltage bias and the catalyst material is deposited selectively on the photo active sites.

In the present work, photochemical deposition of CoAc on ZnO and its activity as a co-catalyst for PEC oxygen evolution are investigated. ZnO nanorods are photoelectrochemically deposited on a conducting glass substrate followed by photochemical deposition of CoAc. A high solubility of Co-salt in acetate buffer solution allows us to study the effect of concentration on photochemical deposition of the co-catalyst as well as on the photoelectrolysis of water. Such a study is not possible involving CoPi due to limited solubility of Co-salts in phosphate buffer solution. The catalytic activity of CoAc-ZnO is greater than CoPi-ZnO reported in the literature.

Experimental

Reagents and materials.— Analytical grade Co(NO3)2, glacial acetic acid (both from S. D. Fine Chemicals), CH3COONa, KH2PO4, K2HPO4 and Zn(NO3)2 (all from Merck) were used as received. All solutions were prepared in doubly distilled water. Acetate buffer solution was prepared by mixing 0.1 M CH3COONa and 0.1 M glacial acetic acid solutions. Similarly, phosphate buffer solution was prepared with double distilled water, acetone and iso-propanol under sonication. Prior to the deposition, CoAc catalyst was chemically and morphologically similar to the photoelectrolysis route adopted by vegetation. A typical example is the photodissociation of water into H2 and O2 using n-type TiO2 photoanode and Pt black cathode was reported by Fujishima and Honda7 in 1972. Following this report, numerous investigations have been reported for photocatalytic and photoelectrochemical water splitting.8 Most of the studies suffer from poor solar to hydrogen conversion efficiency due to fast recombination of photogenerated charge carriers and poor catalytic activity of semiconductor electrodes toward multi-electron oxygen evolution reaction (OER) at the photoanode.9,10 Several metal oxides such as RuO2,11 IrO2,12,13 etc., are coupled with semiconductors (TiO2, ZnO, etc.) as co-catalysts to enhance the sluggish kinetics of water oxidation. However, high cost of Ru and Ir limit their widespread application. Recently, a cobalt-phosphate complex (CoPi) has been reported14 as an inexpensive and efficient catalyst. It has been reported that photoelectrochemical water oxidation is significantly enhanced when the CoPi is interfaced with semiconductor photoanodes such as Si,15 TiO2,16 BiVO4,17,18 WO319 etc., and its activity as a co-catalyst in photoelectrochemical (PEC) OER. Photochemical deposition is preferred to electrodeposition as it does not require any voltage bias and the catalyst material is deposited selectively on the photo active sites.

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Electrochemical deposition of ZnO on FTO.— Prior to the deposition of ZnO, FTO coated glass substrates were cleaned thoroughly with double distilled water, acetone and iso-propanol under sonication for 30 min. in each solvent. Then, Zn(OH)2 was deposited onto FTO coated glass substrate by potentiostatic method.27 The deposition was carried out in a Pyrex glass cell with FTO coated glass, platinum foil and saturated calomel electrode (SCE) as the working, counter and reference electrodes, respectively. A 100 mL aqueous solution containing 5 mM Zn(NO3)2 and 50 mM NaNO3 was taken in a 250 mL glass beaker and heated to 85 °C in a water bath. At first, a layer of Zn(OH)2 was deposited at a -1.3 V vs. SCE for 15 s. Then, the potential was decreased to -1.0 V vs. SCE and the electrolysis was continued for 1800 s. Zn(OH)2 coated electrodes were rinsed with...
water, dried under N₂ flow and heated at 350°C in air to obtain ZnO nanorods (ZnO NRs).

**Photochemical deposition of CoAc on ZnO.**—CoAc was deposited on ZnO nanorods by photochemical method. For this, ZnO deposited FTO glass electrodes were dipped in 0.1 M sodium acetate buffer (pH 7.0) solution containing 0.5 mM Co(NO₃)₂ in a petri dish and illuminated by a high pressure Hg-vapor lamp (125 W) kept at a distance of 15 cm from the electrode. The power of the light at the surface of the electrode was 15 mW cm⁻² as measured by ferrioxalate actinometry. To avoid any heating effect, cold water was circulated. The CoAc-ZnO coated FTO electrodes were washed with double distilled water, dried in air and kept in a desiccator under dark. Several electrodes were prepared by varying the time of illumination and also the concentration of Co(NO₃)₂.

**Physical characterization and photoelectrochemical studies.**—Microscopic analysis was carried out by using Ultra 55 scanning electron microscope (SEM) equipped with EDXA system at 10 kV. Powder X-ray diffraction (XRD) patterns were recorded by Bruker D8 diffractometer using Cu Kα radiation. The surface compositions of the materials were examined by X-ray photoelectron spectroscopy (XPS) using SPECS GmbH spectrometer (Phoibos 100 MCD Energy Analyzer) with Mg Kα radiation (1253.6 eV). The peak of C1s at 284.6 eV was taken as the reference energy position. The optical bandgap was estimated from the UV-Vis diffuse reflectance spectroscopic studies by Perkin Elmer Lambda 750 spectrophotometer with pure BaSO₄ as the reference. Electrochemical impedance spectra were recorded by means of CH Instruments potentiostat/galvanostat model CHI 608C, which was coupled to a frequency response analyzer. An ac perturbation of 5 mV was applied at a frequency of 1 kHz and impedance was measured as a function of potential. For photoelectrochemical characterization studies, a 100 W halogen lamp (Philips lamp model 6834) was used. The output power at the electrode was calibrated as 100 mW cm⁻² (1 Sun) using a standard c-Si solar cell and photodiode power meter (Thorlab, S120B). The temperature of the cell was maintained at 22°C. The electrochemical measurements were performed using PARC EG&G potentiostat/galvanostat model Versastat II in a three-electrode system with the semiconductor working electrode, a Pt foil counter electrode and a SCE reference electrode. The electrolyte was 0.1 M potassium phosphate buffer solution of pH 7.0. For linear sweep voltammograms, the electrodes were scanned from 0.45 to 2.15 V vs. RHE at a sweep rate of 50 mV s⁻¹. Time-dependent photocurrents were measured at various potentials (0.65, 1.05, and 1.45 V vs. RHE) under chopped light condition (pulse width: 15 s). Current density values are reported on the basis of geometrical area of the electrode. All potential values of PEC experiments were converted to reversible hydrogen electrode (RHE) scale and presented unless otherwise stated.

**Results and Discussion**

**Preparation and characterization of ZnO nanorods.**—In the present work, ZnO is employed as the semiconducting substrate since it provides advantages such as good electron mobility, wide availability, relatively less toxicity and easy synthesis of 1D nano architectures such as nanowires and nanorods. ZnO was deposited on FTO coated glass electrodes from an aqueous solution containing 5 mM Zn(NO₃)₂ by cathodic polarization. Due to the reduction of NO₃⁻ to NO₂⁻ ions, there is an increase in OH⁻ concentration at the electrode surface (reaction 1).

\[
\text{NO}_3^- + H_2O + 2e^- \rightarrow \text{NO}_2^- + 2OH^- \tag{1}
\]

This reaction results in the precipitation of Zn(OH)₂ on the electrode surface. On heating at 350°C, Zn(OH)₂ is converted into ZnO. The resulting ZnO was composed of randomly oriented nanorods (Fig. 1a). The average diameter and length of nanorods are 150 nm and 500 nm, respectively. The chemical composition was analyzed using EDXA, XRD and XPS techniques. In the XRD pattern of bare ZnO (Fig. 2ii), five main diffraction peaks corresponding to (102), (110), (103), (201) and (004) planes of ZnO hexagonal wurtzite structure (JCPDS number 36–1451) are identified. All other peaks are assigned to the underlying FTO glass substrate (Fig. 2i). EDXA spectrum for the as prepared ZnO NRs on
Fig. 4a shows the XPS survey spectrum of ZnO NRs on FTO substrate and O as the major elements identified with a uniform distribution. The electrochemical route produced pure ZnO nanostructure with Zn corresponding to Zn 2p1/2 and 2p3/2, which are typical of ZnO. The energy levels of ZnO and the species present in the solutions are shown in Fig. 5b. The valence band edge of ZnO is located at 2.6 V vs. standard hydrogen electrode (SHE), which is more positive than the oxidation potential of water. Since, the oxidation of Co2+ to Co3+ and consequent formation of CoAc occurs at a potential lower than the OER potential (Fig. 5a(i)), it is anticipated that the photogenerated holes in the valence band can also oxidize Co2+ to form CoAc on the surface of illuminated ZnO.

The CoAc catalyst was photochemically deposited on ZnO NRs from 0.1 M acetate buffer solution containing 0.5 mM Co2+ by UV radiation from a high pressure Hg-lamp. SEM image of ZnO after 1 h of photochemical deposition (Fig. 1b) suggests that CoAc catalyst layers are grown on the surface of ZnO NRs. The XRD pattern of CoAc deposited ZnO (Fig. 2ii) matches with that of ZnO (Fig. 2i). No additional peaks are observed indicating amorphous nature of the photochemically deposited CoAc catalyst. After the deposition of CoAc, the EDXA spectrum (Fig. 3d) shows the presence of Co and C in addition to Zn and O. There is a uniform distribution of Co and C (Fig. 3e and 3f). Furthermore, Co/C ratio varies from 1:1 to 1:1.5 (Fig. 3d), which agrees well with the chemical composition of electrochemically deposited CoAc catalyst on FTO coated glass electrodes. Furthermore, the XPS survey spectrum (Fig. 4d) of CoAc-ZnO is identical to that of ZnO but with additional peaks from Co 2p core level and Auger lines by Co LMM transition. In the Co 2p high resolution spectra (Fig. 4e), there are two peaks at binding energies 793.7 and 778.7 eV corresponding Co 2p1/2 and Co 2p3/2, respectively. Additionally, relatively weak and broader shake-up features are also observed in the vicinity of Co 2p main peaks, which indicate the presence of high spin paramagnetic Co(II) species. These results are in agreement with the reported values for electrochemically synthesized CoAc further supporting that photochemically deposited CoAc is chemically identical to electrochemically prepared CoAc catalyst.

Photochemical deposition and characterization of CoAc on ZnO.— Although the electrochemical route produces CoAc on ZnO surface, photochemical deposition is preferred because of the deposition of the co-catalyst selectively on the surface of photoactive ZnO layer. In general, photochemical technique can be used only if the semiconducting substrate has suitable band position with respect to the oxidation of Co2+/Co3+. The energy levels of ZnO and the species present in the solutions are shown in Fig. 5b. The valence band edge of ZnO is located at 2.6 V vs. standard hydrogen electrode (SHE), which is more positive than the oxidation potential of water. Since, the oxidation of Co2+ to Co3+ and consequent formation of CoAc occurs at a potential lower than the OER potential (Fig. 5a(i)), it is anticipated that the photogenerated holes in the valence band can also oxidize Co2+ to form CoAc on the surface of illuminated ZnO.

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Photoelectrochemical OER studies on CoAc-ZnO.— Photocurrent-potential characteristics ZnO NRs electrodes with and without CoAc were studied in 0.1 M phosphate buffer solution (pH 7.0). Phosphate buffer was used because the CoAc catalyst displays greater catalytic activity in phosphate electrolyte than in acetate solution. At first, ZnO-FTO was subjected to linear potential sweep at 50 mV s−1 in the potential range from 0.40 to 2.15 V vs. RHE under dark condition. Fig. 6a(i) shows the corresponding voltammogram. It is seen that there is no significant current upto 1.75 V vs. RHE in the dark indicating the absence of any electrochemical reaction. Increase in the current above 1.75 V vs. RHE is caused by the electrochemical OER. On the contrary, under illumination by a halogen lamp (Fig. 6a(ii)), current flow starts at a potential as low as 0.50 V vs. RHE due to n-type nature of ZnO. However, current density value is only 25 μA cm−2 at 1.23 V vs. RHE and it reaches 32 μA cm−2 at 1.65 V vs. RHE. A poor photocurrent density is attributed to rapid recombination of charge carriers and sluggish charge-transfer reactions at the ZnO-electrolyte interface. Hence, it was anticipated that CoAc co-catalyst could enhance the rate of interfacial reaction by reducing the charge carrier.
Figure 4. XPS data of ZnO (a-c) before CoAc deposition and (d, e) after CoAc deposition. Here, (a and d) survey spectrum, (b) Zn 2p, (c) O 1s and (e) Co 2p detailed spectra.

recombination and therefor a significant current could flow under illumination. It is seen in Fig. 6a(iii) that, there is no anodic current flow at CoAc-ZnO electrode until potential reaches 1.75 V vs. RHE in dark and current increases at potentials greater than 1.75 V vs. RHE due to electrochemical OER similar to ZnO electrode (Fig. 6a(i)). It is worth noticing that the hybrid CoAc-ZnO electrode exhibits greater electrochemical activity than the ZnO electrode under dark electrolysis condition (above 1.75 V vs. RHE). Current density value at 2.15 V vs. RHE is 58 μA cm⁻² on ZnO, whereas it is almost twice on CoAc-ZnO. This is due to greater catalytic activity of CoAc than ZnO for electrochemical OER. Under light condition (Fig. 6a(iv)), current starts flowing at a potential as low as 0.50 V vs. RHE similar in the case of ZnO. Current reaches a value of 85 μA cm⁻² at 1.23 V vs. RHE and 92 μA cm⁻² at 1.65 V vs. RHE. These values are greater by 3.4 and 2.8 times, respectively, in comparison with the current measured for ZnO indicating the positive influence of CoAc toward photooxidation of water. It should be noted that CoAc has pronounced effect at lower voltage, where the charge carrier recombination is the

Figure 5. (a) Cyclic voltammograms of ZnO coated FTO glass slides in 0.1 M acetate solution (i) with 10 mM Co²⁺ and (ii) without Co²⁺ at a sweep rate of 50 mVs⁻¹, and (b) relevant energy levels.
current limiting factor. To rule out the possibility that CoAc itself is photoactive, CoAc was electrochemically deposited on FTO glass and linear sweep voltammograms were recorded in neutral phosphate electrolyte under dark (Fig. 6b(i)) and light condition (Fig. 6b(ii)). It is seen that CoAc alone is inactive toward photooxidation. These results suggest that CoAc acts as a co-catalyst when interfaced with ZnO semiconductor.

Detection of oxygen using Pt electrode.— The evolved O2 was probed by electrochemical oxygen reduction reaction (ORR) on a Pt electrode. An air-tight electrochemical cell with a cleaned Pt foil and a ZnO electrode as the working electrodes for ORR and OER, respectively, was used. The cell was filled with phosphate buffer electrolyte and purged with high purity Ar-gas for 2 h. Then, the Pt electrode was subjected to linear sweep voltammetry (LSV) from 0.80 to 0.28 V vs. RHE at 50 mV s\(^{-1}\). Negligibly small current flows and a very small current peak appears at 0.42 V vs. RHE due to the reduction of trace amount of dissolved oxygen (Fig. 7i). Then, the photoelectrolysis was conducted at ZnO under illumination at 1.23 V vs. RHE. After 1 h, photoelectrochemical reaction was stopped and Pt electrode was subjected to LSV again. The current peak at 0.42 V vs. RHE due to ORR is significantly enhanced (Fig. 7ii), indicating that photoelectrochemical reaction on ZnO generated O2. Experiments were repeated using CoAc-ZnO electrode in the place of ZnO. It is clear from Fig. 7iii that the reduction peak at 0.42 V vs. RHE is more intense in comparison with that of bare ZnO. This is due to high oxygen evolution reaction rate on CoAc-ZnO. The current peak at 0.42 V vs. RHE is confirmed as sue to ORR by purging with pure O2 from a cylinder (Fig. 7iv).

Effect of thickness of CoAc on ZnO.— To study the effect of CoAc loading, CoAc of different thicknesses were deposited photochemically by varying the illumination time in a solution of 0.1 M acetate buffer containing 0.5 mM Co(NO\(_3\))\(_2\). The electrodes are referred to as CoAc-10, CoAc-20 and CoAc-30 for the CoAc deposited for 10, 20 and 30 minutes, respectively. The electrodes were then subjected to constant potential electrolysis under chopped light condition (100 mW cm\(^{-2}\), pulse width: 15 s) at different potentials: 0.65 (Fig. 8a), 1.05 (Fig. 8b) and 1.45 V (Fig. 8c) vs. RHE. It is seen from Fig. 8a that photocurrent density is the least for bare ZnO (Fig. 8a(i)), which is 0.4 \(\mu\)A cm\(^{-2}\). It increases to 3.5 \(\mu\)A cm\(^{-2}\) for CoAc-10 (Fig. 8a(ii)) and 12.5 \(\mu\)A cm\(^{-2}\) for CoAc-20 (Fig. 8a(iii)). Further increase in the CoAc deposition time to 30 minute results a decrease in the photocurrent to 6.6 \(\mu\)A cm\(^{-2}\) (Fig. 8a(iv)). This decrease could be due to absorption or scattering of light by a thick and opaque CoAc layer. Moreover, the excess CoAc deposit can also act as the electron trap sites, further facilitating the charge carrier recombination at the semiconductor surface. Hence, a deposition time of 20 minute is the optimum for photooxidation under the present experimental condition. At 1.05 V vs. RHE, ZnO gives a photocurrent of around 15.1 \(\mu\)A cm\(^{-2}\) (Fig. 8b(i)) whereas it is 21.5 (Fig. 8b(ii)), 50.6 (Fig. 8b(iii)) and 34.9 \(\mu\)A cm\(^{-2}\) (Fig. 8b(iv)), respectively, for CoAc-10, CoAc-20 and CoAc-30. Similar observations are made at 1.45 V vs. RHE (Fig. 8c) with photocurrent density values of 25.6, 41.1, 64.2 and 50.1 \(\mu\)A cm\(^{-2}\) measured at ZnO, CoAc-10, CoAc-20 and CoAc-30 electrodes. The variation in the photocurrent density with CoAc deposition time is plotted for 0.65 (Fig. 9a(i)) and 1.05 V (Fig. 9a(ii)) vs. RHE. If the illumination time is small, the quantity

![Figure 6](image-url)

**Figure 6.** (a) Linear sweep voltammograms of ZnO under (i) dark and (ii) light and of CoAc-ZnO in (iii) dark and (iv) light in 0.1 M phosphate (pH 7.0) electrolyte. Sweep rate: 50 mV s\(^{-1}\). Photodeposition was carried out for 20 min from 0.1 M acetate solution (pH 7.0) containing 0.5 mM Co\(^{2+}\). (b) Linear sweep voltammograms of electrochemically deposited CoAc on FTO glass in 0.1 M phosphate electrolyte (pH 7.0) under (i) dark and (ii) light conditions. CoAc was deposited at 1.05 V vs. SCE for 30 minute from 0.5 mM Co\(^{2+}\) in 0.1 M acetate buffer (pH 7.0). Sweep rate: 5 mV s\(^{-1}\).

![Figure 7](image-url)

**Figure 7.** Linear sweep voltammograms of O2 reduction reaction on a Pt electrode in 0.1 M neutral phosphate electrolyte under (i) Ar-purged condition and after 1 h of generating O2 by photoelectrolysis at 1.23 V vs. RHE using (ii) ZnO, (iii) CoAc loaded ZnO and (iv) after purging with oxygen from a cylinder. Sweep rate: 50 mV s\(^{-1}\).
Figure 8. Photocurrent density of (i) ZnO, (ii) CoAc-10, (iii) CoAc-20 and (iv) CoAc-30 electrodes measured at (a) 0.65, (b) 1.05 and (c) 1.45 V vs. RHE. Here, CoAc-10 implies that CoAc was deposited for 10 minute and so on. Incident light power 100 mWcm$^{-2}$ and pulse width 15 s.

Figure 9. (a) Variation in the steady state photocurrent density with the deposition time of CoAc on ZnO at potential of (i) 0.65 and (ii) 1.05 V vs. RHE. (b) Current density vs. time plot for CoAc-ZnO measured at 1.23 V vs. RHE in 0.1 M phosphate (pH 7.0) electrolyte under (i) dark and (ii) light. Incident light power 100 mWcm$^{-2}$. CoAc was photochemically deposited from 0.5 mM Co$^{2+}$ + 0.1 M acetate buffer solution (pH 7.0) for 20 minute by UV illumination.
of CoAc deposited may not be sufficient to cover the entire surface of ZnO NR arrays. If the deposition time is long, very dense and opaque layers of CoAc are formed which may block or scatter the light. Consequently the resulting photo response is lower. Hence, the best performance is obtained for CoAc-20 with 3.4 and 2.5 times enhancement in the photocurrent, respectively, at 1.05 and 1.45 V vs. RHE. Similar to these studies, CoPi loaded ZnO was reported for photoelectrochemical water oxidation in neutral phosphate buffer electrolyte.\textsuperscript{34} Around 1.5 fold increase in the current was observed at 0.2 V vs. SCE. Similarly, photochemical deposition of NiBi on ZnO was also reported recently.\textsuperscript{35} The authors found that NiBi was better than CoPi as the former improved the photocurrent more than 1.9 times while the later increased only 1.2 fold at 1.0 V vs. RHE. Photoelectrochemical activity of CoPi-ZnO was also studied in an alkaline medium.\textsuperscript{36} The photocurrents measured at 0.2 V vs. Ag/AgCl, Cl\textsuperscript{-} showed that the presence of CoPi catalyst enhanced the steady-state photocurrent by 1.5 times in comparison with bare ZnO. Thus, the photocurrent improvement observed for the CoAc catalyst in the present study is superior to the literature reports on similar studies using NiBi or CoPi. This is anticipated as the intrinsic catalytic activity of CoAc is greater than that of CoPi for OER.\textsuperscript{25,26} In addition, the stability of CoAc deposited ZnO was investigated at a constant bias of 1.23 V vs. RHE for 1 h under dark (Fig. 9b(ii)) and light (Fig. 9b(i)) conditions. The electrode exhibited excellent stability and retained around 90\% photocurrent at the end of the experiment.

**Effect of concentration of Co\textsuperscript{2+} ion on photochemical deposition of CoAc.**— It was further intended to examine the effect of concentration of Co\textsuperscript{2+} on photochemical deposition of CoAc on ZnO. For this, experiments were repeated at various concentrations of Co\textsuperscript{2+} ranging from 0.5 mM to 5 mM. To avoid excessive deposition, illumination time was restricted to 3 minute. Catalytic activity was studied by linear sweep voltammetry at 50 mV s\textsuperscript{-1} in neutral phosphate electrolyte under illumination by a halogen lamp (Fig. 10). The effect of concentration of Co\textsuperscript{2+} on both photochemical deposition and the catalytic activity toward OER was observed. It is seen from Fig. 10 that current density value at 1.65 V vs. RHE is 48 $\mu$A cm\textsuperscript{-2} for the CoAc deposited from 0.5 mM (Fig. 10v), whereas it is almost three times higher for the CoAc deposited from 3 mM (Fig. 10v). Additionally, this current value is greater than 100 $\mu$A cm\textsuperscript{-2} obtained for the electrode prepared from 0.5 mM Co\textsuperscript{2+} solution by 20 min illumination (Fig. 10v). These results indicate that the deposition time can be significantly reduced at higher concentrations of Co\textsuperscript{2+}. This result is in contrast with photochemical deposition form phosphate or borate buffer electrolytes in which solubility of Co\textsuperscript{2+} is limited to 0.5 mM. Nevertheless, an increase in the concentration of Co\textsuperscript{2+} beyond 3 mM (Fig. 10v and 10vi), results in a sharp decrease in the photocurrent. The reason could be a partial blockage of radiation by excessive CoAc on the surface of ZnO, which results in a decreased photoresponse.

**Effect of addition of Na\textsubscript{2}SO\textsubscript{3} on photoelectrochemical behavior.—** To further confirm that sluggish water oxidation kinetics are responsible for low photoelectrochemical current in the case of ZnO, sodium sulfite (0.5 M) was added into the phosphate electrolyte (pH was maintained at 7.0) as a hole scavenger. Sodium sulfite was chosen because the oxidation of sulfite is thermodynamically and kinetically more favorable than water oxidation.\textsuperscript{37} Fig. 11 shows the effect of Na\textsubscript{2}SO\textsubscript{3} during electrolysis at 0.65 V vs. RHE. It is seen in Fig. 11i and 11ii that photocurrent density of 4.5 $\mu$A cm\textsuperscript{-2} is obtained for bare ZnO after adding 0.5 M Na\textsubscript{2}SO\textsubscript{3} which is much higher than the current value (1 $\mu$A cm\textsuperscript{-2}) obtained without Na\textsubscript{2}SO\textsubscript{3}. This shows that poor kinetics is the one of the current limiting factors in the case of ZnO during photooxidation of water. Similar experiments were repeated using CoAc loaded ZnO (Fig. 11iii and 11iv). Interestingly, there is no significant improvement in current after the addition of Na\textsubscript{2}SO\textsubscript{3}. These results clearly suggest that in the presence of CoAc, the photocurrent value is not limited by the reaction kinetics, signifying the role of CoAc as an efficient co-catalyst toward photo oxidation of water.

**Band gap measurements.—** It is also appropriate to determine whether the cathodic shift in the OER onset potential and subsequent improvement in the photocurrent produced by CoAc deposition is related to any change in the bandgap or band positions of ZnO semiconductor. To rule out the possibility of bandgap shift, diffuse reflectance spectra were recorded for ZnO electrodes before (Fig. 12a(i)) and after 20 (Fig. 12a(ii)) and 60 minute (Fig. 12a(iii)) of CoAc deposition from 0.1 M acetate solutions (pH 7.0) containing 0.5 mM Co\textsuperscript{2+}. It is evident from Fig. 12a that the bandgap of ZnO remains the same (3.25 eV) before and after CoAc deposition. Hence, improved photoresponse is not due to any shift in the bandgap. On the other hand, CoAc deposition causes a slightly reduced reflectance values in the visible region especially at higher loading level (Fig. 12a(iii)), probably due to absorption of incident light by the brownish black coating of CoAc. This further supports our assumption that poor photoresponse at higher CoAc loading level is due to the loss of effective radiation reaching at the semiconductor photoanode. It was further intended to
probe any shift in the conduction band of ZnO by CoAc deposition as it could be another reason for higher catalytic performance. For an n-type semiconductor, the flatband potential (E_FB) can be considered as approximately the same as the conduction band potential. Hence, measuring E_FB of ZnO before and after CoAc deposition can directly give an idea regarding possible shift in the conduction band. Generally, the flatband potential is determined by measuring the capacitance (C) at different electrode potential (V) using the following equation,

\[
\frac{1}{C^2} = \frac{1}{\varepsilon_0 \varepsilon_r N_d} [V - V_{fb} - (k_B T/e)]
\]

where e is the elementary charge, \(\varepsilon_r\) is the dielectric constant of the semiconductor, \(\varepsilon_0\) is the permittivity of air, \(N_d\) is the donor density, V is the applied potential and \(V_{fb}\) is the flatband potential. Thus, the x-intercept of the linear region of the Mott–Schottky plot (1/C^2 vs. V) provides the flatband potential of the corresponding electrode. Accordingly, we examined the behavior of the bulk capacitance of ZnO and CoAc decorated ZnO electrodes as a function of potential using electrochemical impedance spectroscopy technique and the resulting Mott–Schottky plots are shown in Fig. 12b. The measured value of flatband potential (E_FB) for ZnO is 0.45 V vs. RHE (Fig. 12b(i)) which is in good agreement with the reported values for electrochemically prepared ZnO nanorods.\(^{38}\) It is inferred from Fig. 12b(ii) that CoAc deposition does not alter the flatband potential. A similar behavior was also observed upon deposition of the Ir\(^{39}\) and Co\(^{40}\) based co-catalysts on hematite photoanodes. These experiments clearly indicate that the improved photocurrent observed in the presence of CoAc deposition on ZnO is not due to any modification in the bandgap or band positions of the ZnO substrate. Therefore, we anticipate that higher photocurrent is the direct consequence of a fast charge transport across the photoanode-electrolyte interface and subsequent reduction in the charge carrier recombination. Here, CoAc acts like a fast redox mediator that shuttles among different oxidation states. It quickly accepts holes from the illuminated semiconductor, undergoes a fast oxidation and finally reduces back to original state along with evolution of oxygen by the oxidation water.

**Mechanism of OER on Co-Ac deposited ZnO.—** Mechanism of OER on Co-Ac deposited ZnO is illustrated in Scheme 1. Illumination of semiconductor produces electron-hole pairs. Electrons in the conduction band are easily transported to external circuit under applied potential. Although, the valence band holes of ZnO can directly oxidize water, ZnO has lower catalytic activity for water oxidation. Hence, in the absence of a suitable co-catalyst such as Co-Ac, these holes may recombine with electrons without causing any reaction. On the other hand, in the presence Co-Ac, the Co(III/II) centers in the catalyst rapidly accept the holes before recombining with electrons to form Co(IV/III) unit and consequently charge separation is improved. Thermodynamically, the oxidation power of the so formed Co(IV/III) is higher enough to oxidize water. Therefore, an immediate evolution of gas is observed as the result of water oxidation.

**Conclusions**

In summary, it is successfully demonstrated for the first time that the photochemical deposition route can be employed to interface the CoAc water oxidation catalyst with a semiconducting photoanode of ZnO nanorods. The photochemical method ensured the selective deposition of CoAc only on photoactive regions unlike in the case of electrochemical deposition. There is about 2.5 times increase in the current at 1.45 V vs. RHE on CoAc-ZnO in relation to the bare ZnO. This result is significantly superior to CoPi-ZnO, which enhances the photocatalytic activity by 1.5 times in relation to bare ZnO.

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**Figure 12.** (a). Diffuse reflectance spectra for ZnO (i) before CoAc deposition and after photodeposition for (ii) 20 and (iii) 40 minute. Photodeposition was done from 0.1 M acetate buffer (pH 7.0) solution containing 0.5 mM Co\(^{2+}\). (b). Mott–Schottky plots of (i) ZnO and (ii) CoAc-ZnO in 0.1 M phosphate electrolyte (pH 7.0) at 1 kHz frequency in the dark. Intercept of the linear region on the x axis is 0.45 V vs. RHE, which is associated with the flatband potential.

**Scheme 1.** Schematic illustration for the mechanism of oxygen evolution reaction on CoAc-ZnO.
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