Nitrogen and Cobalt co-doped Zinc Oxide nanowires – viable photoanodes for hydrogen generation via photoelectrochemical water splitting

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42 **Abstract:**
43 Photoelectrochemical (PEC) water splitting has been considered a promising and
44 environmentally benign approach for efficient and economic hydrogen generation by utilization
45 of solar energy. Development of semiconductor materials with low band gap, high
46 photoelectrochemical activity and stability has been of particular interest for a viable PEC water
47 splitting system. In this study, Co doped ZnO, .i.e., (Zn_{0.95}Co_{0.05})O nanowires (NWs) was

selected as the composition for co-doping with nitrogen by comparing solar to hydrogen efficiency (SHE) of ZnO NWs with that of various compositions of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$). Further, nanostructured vertically aligned Co and N-doped ZnO, .i.e., $(\text{Zn}_{1-x}\text{Co}_x)\text{O:N}$ NWs ($x=0.05$) have been studied as photoanodes for PEC water splitting. An optimal SHE of 1.39% was obtained for the doped NWs generated at 600°C in ammonia atmosphere, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs, the highest reported thus far to the best of our knowledge for ZnO based photoanodes. Further, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs exhibited excellent photoelectrochemical stability under illumination compared to pure ZnO NWs. These promising results thus suggest the potential of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs as a viable photoanode in PEC water splitting cell. Additionally, theoretical first principles study explains the beneficial effects of Co and N co-doping on band gap and electronic structure of ZnO.

Keywords:

Photoelectrochemical water splitting; nanowires; hydrothermal; cobalt doping; doped zinc oxide; nitrogen doping

1. Introduction:

The ever increasing dependence on fossil fuels as the primary energy source has contributed to severe environmental consequences warranting exploration of renewable and clean energy sources and thus, potentially lowering the dependence on fossil fuels, in turn aiming to solve the global energy crisis.[1-5] Hence, generation of electricity from renewable energy sources, such as solar, wind has received much attention for meeting the future energy demand

since these approaches boast of the single major attribute of not generating carbon dioxide as a by-product, a major undesirable greenhouse pollutant.[2, 6-10] Solar energy is a de-concentrated and illimitable natural energy reservoir and thus, considered as an attractive approach for solving the global energy crisis.[7] Due to the sporadic nature of solar energy, it is important however, to convert solar energy into a clean non-carbonaceous fuel, which will offer the advantages of economical storage and distribution.[7]

Hydrogen has been long considered as a promising energy source to replace gasoline for meeting global energy demand, due to its high energy density (120 MJ/kg for H₂ higher than 44.4 MJ/kg for Gasoline) and environmentally benign nature (low carbon footprint).[4, 5] However, economic production, along with cost effective storage and distribution are the major roadblocks in the commercialization of hydrogen as a fuel.[4, 5] Currently, the production of hydrogen on the industrial scale involves steam reforming of natural gas, which requires high operating temperatures (700°C-1000°C), moreover producing CO₂-an undesired greenhouse pollutant.[8, 10] Hence, production of H₂ from non-fossil fuel resources such as water is very much desired, as it does not produce any carbonaceous pollutants.[7, 8, 10] However, splitting of water for H₂ production is an uphill proposition, requiring external energy ($\Delta G^{\circ}=237.13 \text{ kJ mol}^{-1}$).[11] Thermolysis of water uses high temperature ($\geq 1000^{\circ}\text{C}$) to overcome this reaction barrier. Moreover, the energy-intensive nature and risk of back reaction of H₂ and O₂ at high operating temperature is a serious concern, which needs to be addressed for its adaptation on industrial scale.[12] Despite these major issues, there has been significant research efforts directed at hydrogen production using alkaline, neutral and proton exchange membrane (PEM) based water electrolysis.[13-21] Though these approaches seem promising as it does not involve greenhouse gas emissions and toxic byproducts, the high capital costs due to the use of

expensive noble metal electro-catalysts (e.g. IrO₂, RuO₂, Pt) and use of electrical energy are major constraints for achieving the targeted hydrogen production cost of \$2.00-\$3.00/kg, which includes production, delivery as well as dispensation.[13, 14, 16-24] As mentioned earlier, solar energy is an economic and viable natural energy source and thus, can be utilized as an external energy source for the water splitting (1.23 eV).

Solar energy induced water splitting, also known as photoelectrochemical (PEC) water splitting is considered as an attractive and environmentally benign approach, since it involves generation of hydrogen from electricity generated by efficient use of semiconductors in a single system.[12] Fujishima and Honda's first pioneer work on PEC water splitting using n-type TiO₂ semiconductor has catapulted PEC water splitting using semiconductor materials among the forerunners for economic production of hydrogen in an environmentally benign manner.[9, 25]

The major regime of the solar spectrum consists of visible light (~46%) with ~4% contribution from UV radiation.[9] Hence, it is important to explore and find a stable and active semiconductor material with high absorption capability in the visible region, for large scale production of H₂ from PEC water splitting. The main criteria for photoelectrode materials are (a) narrow band gap (1.23 eV < E_g < 3 eV), (b) high electrical conductivity, (c) high photoelectrochemical stability in the electrolyte solution and (d) suitable band structure such that oxidation (1.23V) and reduction potential of water (0V) lie within the band gap of the material.[9] TiO₂ has been largely explored extensively among other light active metal oxide semiconductors. However, the poor electrical conductivity of TiO₂ is one of the major constraints for its use in commercialization PEC water splitting cells.[26-29] Other metal oxide

semiconductors such as ZnO, WO₃ and Fe₂O₃ have also been widely studied as photoanodes for PEC cells due to their low cost and easy availability for large scale production.[7, 30-34]

Among these myriad semiconductors, ZnO is considered as a very promising material for hydrogen generation from PEC water splitting due to its higher electron mobility than TiO₂ ($\sim 155 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for ZnO *vs* $\sim 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for TiO₂).[35-40] However, the wide band gap ($\sim 3.2 \text{ eV}$) and poor stability of ZnO in the aqueous electrolyte solution result in poor absorption of light and thus, poor photoelectrochemical activity for PEC water splitting.[41] This problem has been recently addressed mainly by tailoring the ZnO electronic structure transforming the band gap to smaller values by doping the structure with metal/non-metal dopant.[41-45] Such a doping strategy is expected to improve photoelectrochemical performance due to improved light absorption occurring as a result of a decrease in the band gap and increase in number of carriers. However, the selection of suitable dopants and their concentration is important for tailoring the band structure of ZnO. Though high concentrations of dopant can offer improved light absorption due to decrease in the band gap, the additional defect levels contributed by dopants in the electronic structure of ZnO can act as recombination sites for photogenerated electron-hole pairs, which results in poor PEC performance and thus, low solar to hydrogen efficiency (SHE), in comparison to undoped ZnO.[46] There has been pioneering research of late conducted into the identification of suitable dopants (such as Cu, N, H, Al, C) for ZnO to achieve superior photoelectrochemical activity for PEC water splitting. The maximum SHE achieved for ZnO based semiconductor material is however only 0.75% for carbon-doped ZnO porous nanoarchitectures.[47] In the aim of attempting to commercialize PEC water splitting for economic production of hydrogen, it is important to improve SHE beyond 0.75%.[48, 49] This

necessitates the identification of other suitable dopants and doped compositions to significantly improve the photoelectrochemical properties of ZnO photoanodes.

Cobalt is considered herein as a promising dopant for ZnO, on the grounds of observed red-shift in the light absorption to the visible region of interest upon doping and thus, portending improved photocatalytic activity.[50, 51] Co doping in ZnO crystal lattice is expected to contribute additional Co-3d electronic states in the band gap of ZnO leading to decreased band gap of ZnO. Moreover, since the ionic radius of Co^{2+} ($\sim 0.56 \text{ \AA}$) is closer to Zn^{2+} ($\sim 0.6 \text{ \AA}$), Co^{2+} can be envisaged to easily enter the ZnO crystal lattice and may easily substitute Zn^{2+} sites in the ZnO crystal lattice contributing to minimum lattice strain.[50, 52] However, beyond an optimum concentration of Co, additional Co-3d states can facilitate recombination of photogenerated carriers.[50, 51, 53] Hence, we attempted to study first, photoelectrochemical activity of undoped and Co doped ZnO nanowires, denoted as $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$), coated on fluorine doped tin oxide (FTO) glass slides. The nanowire geometry is chosen, on the grounds of its known advantages which include high surface area which provides large area of electrolyte-electrode contact and efficient path for transport of photogenerated carriers in the material.[54-56] Increased density of oriented crystallites in a specific direction offers reduced grain boundaries leading to reduced grain boundary scattering of charge carriers and thus, efficient carrier transport to the external circuit.[54, 55] This has been confirmed by improved activity for PEC water splitting exhibited by carbon doped ZnO nanowires and hydrogen doped ZnO nanowires grown in (002) direction.[27, 57, 58]

The photoelectrochemical activity of the selected composition $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0.05$), based on the results of photoelectrochemical characterization discussed later, is further improved by N-doping in $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0.05$). The study of nitrogen doped TiO_2 by

Hoang et al. has demonstrated that nitrogen is a potential anionic dopant for TiO_2 [59], wherein N-doping in TiO_2 offered improved carrier density, reduced band gap with improved light absorption in the visible region of interest, improved charge separation, transport and collection and improved SHE, compared to pure TiO_2 . The improved photo-response after N doping in TiO_2 can be attributed to the introduction of N 2p states near valence band edge of TiO_2 , which contributed to lowering the band gap. The N 2p orbital has higher potential energy than the O 2p orbital in ZnO.[11] Thus when N atoms are substituted for O atoms in ZnO, the HOMO (highest occupied molecular orbital) of the material is expected to shift higher without affecting the level of the bottom of the conduction band (i.e., lowest unoccupied molecular orbital, LUMO), which will help in lowering the band gap of ZnO.[11] Following this strategy, N doping is carried out for the selected composition of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0.05$). The N-doping is carried out for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs by heat treating the structures in NH_3 at different temperatures, 400°C , 500°C , 600°C and 700°C , to achieve the desired N-doping benefits with different concentration of nitrogen and also, to reduce the band gap further, compared to $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs[60, 61], with the aim of achieving high solar to hydrogen efficiency (SHE). The heat treatment at different temperatures in NH_3 atmosphere has been carried out to relate PEC performance as photoanode with different concentration of nitrogen and thus, to study the role of dopants in altering the electronic structure of ZnO and consequently, improving the desired photoelectrochemical activity of doped ZnO NWs.

In this work, theoretical first principles calculations have also been carried out to augment and support the experimental findings by studying the effects of Co- and N co-doping on the electronic structure of ZnO in general, and also on the optical band gap width in particular. To the best of our knowledge and the reported literature information, no reports exist

on Co and N doped ZnO nanowires (NWs), i.e., $(\text{Zn}_{1-x}\text{Co}_x)\text{O:N}$ NWs synthesized by a simple hydrothermal route on FTO slides and study of their activity as photoanode for PEC water splitting with consideration of different concentration of dopants (Co and N). Hence, the present report documents the experimental and theoretical studies conducted for assessing the photoelectrochemical (PEC) performance of $(\text{Zn}_{1-x}\text{Co}_x)\text{O:N}$ NWs with the overall goal of this system exhibiting efficient hydrogen generation and thus achieve a high SHE from PEC water splitting. As a result, the system could be considered as a potential promising photoanode for PEC water splitting for efficient hydrogen generation.

2. Experimental:

2.1 Synthesis of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$):

$(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs were synthesized by the well-known hydrothermal method onto a zinc oxide seed layer deposited onto fluorine-doped tin oxide (FTO) coated glass substrate[30, 54, 62-64]. Prior to growing the nanowires, the FTO coated glass substrate (0.5cm×2.5cm, Aldrich) was thoroughly cleaned by ultrasonication in acetone, ethanol and deionized water. 5.5 mM zinc acetate solution in ethanol (anhydrous, 200 proof, 99.5+%, Aldrich) was spin-coated on cleaned FTO substrate (Specialty coating Systems Inc., Model P6712) at 500 rpm for 40 sec and then heated at 125°C. The heating step formed zinc acetate layer on the substrate. The spin coating process was repeated a second time followed by heating at 125°C. The ZnO seed layer was thus formed by heat treatment of FTO slide with zinc acetate layer, in air at 340°C for 20 min.

The seed layer coated FTO substrate was then placed with conductive surface down in a sealed hydrothermal container containing the growth solution of zinc nitrate hexahydrate (0.05

M, Alfa Aesar), cobalt acetate tetrahydrate (Aldrich), hexamethylenetetramine (HMTA, 0.025 M, Alfa Aesar), polyethylenimine (5.0 mM, end-capped, molecular weight 800 g mol⁻¹ LS, Aldrich) and ammonium hydroxide (0.35 M). The composition of cobalt acetate tetrahydrate was varied in accordance with the desired Co (dopant) concentration. Following this, the sealed container was placed in a water bath, preheated to 90°C for 6 h. The resulting nanowires were then thoroughly rinsed with ethanol and D.I. water, purified by the Milli-Q system (18MΩ cm deionized water, Milli-Q Academic, Millipore), followed by drying at 50°C for 6 h. To compare results with undoped ZnO, ZnO NWs were also synthesized by following the same procedure, without the addition of cobalt acetate tetrahydrate in the growth solution. The concentration of Co used was 5 and 10 at.% and these compositions are denoted as (Zn_{0.95}Co_{0.05})O and (Zn_{0.9}Co_{0.1})O NWs in this study, respectively.

2.2 Synthesis of (Zn_{1-x}Co_x)O:N NWs (x=0.05):

(Zn_{1-x}Co_x)O NWs (x=0.05) were selected for N doping and were accordingly grown on FTO substrate following the same procedure as mentioned above. The Co-doped ZnO NWs were heat-treated for 1 h at 400°C, 500°C, 600°C and 700°C in anhydrous NH₃ atmosphere (Matheson: 99.99%, flow rate=100cm³/min) using a ramp rate of 10°C/min. (Zn_{1-x}Co_x)O NWs (x=0.05), heat-treated in NH₃ at 400°C, 500°C, 600°C and 700°C are accordingly denoted as (Zn_{0.95}Co_{0.05})O:N-400 NWs, (Zn_{0.95}Co_{0.05})O:N-500 NWs, (Zn_{0.95}Co_{0.05})O:N-600 NWs and (Zn_{0.95}Co_{0.05})O:N-700 NWs throughout this study, respectively.

The experimental details of structural characterization and photoelectrochemical study of materials as well as the details of computational methodology are given in **supporting information (Section S1)**.

3. Results and discussion:

3.1 Synthesis and characterization of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$)

The doping strategy is expected to improve light absorption of ZnO NWs in the visible range due to a decrease in the band gap, in comparison to undoped ZnO NWs. As mentioned earlier, beyond an optimum concentration of the dopant, the additional electronic levels of the dopant can facilitate recombination of photogenerated carriers, resulting in poor photoelectrochemical activity of doped ZnO NWs.[46] In this context, $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0.05, 0.1$), were synthesized by hydrothermal approach and tested as a photoanode to select a suitable concentration of cobalt, which will offer improved light absorption due to a reduction in the band gap and consequently result in superior photoelectrochemical activity with minimum recombination of carriers, in comparison to undoped ZnO NWs. The structural characterization of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs is correspondingly discussed in **Section S2**.

UV-vis absorbance and Tauc analysis of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$)

The optical properties of undoped ZnO and $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs were studied using UV-vis absorption spectroscopy. UV-vis absorption spectra of ZnO and $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0.05, 0.1$) are shown in **Fig. 1a**. The onset of light absorption for pure ZnO NWs is seen at ~450 nm, which is similar to that reported earlier.[30, 50, 51] The absorption of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs is red-shifted to longer wavelengths and correspondingly, lower band gaps compared to pure ZnO NWs. It is

noteworthy that $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0.05, 0.1$) show ~68% and ~81% improved light absorption at 500 nm, in comparison to undoped ZnO NWs and the light absorption in the visible region increases with increase in Co concentration, respectively. 500 nm is chosen for comparison of the absorbance of the semiconductor materials in this study, as it is close to the wavelength at which maximum solar irradiance is obtained.[65] The improved light absorption in the visible region can be attributed to decrease in the band gap due to the appearance of Co-3d electronic states within the Fermi level vicinity for $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0.05, 0.1$) (discussed in detail later in the results of the theoretical study). Tauc analysis was subsequently carried out for the estimation of the band gap of ZnO and $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs, shown in **Fig. 1b**. The optical band gap of the $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs is estimated from the x-intercept of the $(\alpha h\nu)^2$ vs $h\nu$ curves. The results of the Tauc analysis for band gap estimation are shown in **Table 2**. A reduction in band gap of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs is observed with increase in Co concentration. The reduction in the band gap of ZnO NWs is important since this facilitates maximum light absorption. This in turn, results in high number of photogenerated electrons available for the reaction, which helps in achieving a marked improvement in the photoelectrochemical (PEC) performance.

Mott-Schottky analysis of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$)

The Mott-Schottky plot of ZnO and $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs are shown in **Fig. 2**. The flat band potential (V_{FB}) of undoped and doped ZnO NWs is found from the x-intercept in Mott-Schottky plots ($1/C^2$ vs V). For undoped ZnO NWs, V_{FB} is ~(-0.5 V vs NHE), which is closer to the value reported earlier.[27] V_{FB} for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ and $(\text{Zn}_{0.9}\text{Co}_{0.1})\text{O}$ NWs are ~(-0.55 V vs NHE) and ~(-0.58 V vs NHE), respectively. In this study, the electrochemical impedance measurements

were conducted at pH=7, which corresponds to $E_h = -0.413$ V (vs NHE) (**Section S2**). Thus, the values of V_{FB} of ZnO and $(Zn_{1-x}Co_x)O$ NWs of different compositions are more negative (cathodic) than the calculated V_{FB} of -0.413 V (vs NHE). This shows that the band edges of $(Zn_{1-x}Co_x)O$ NWs straddle the reduction potential of water (0 V vs NHE). The positive slope obtained in Mott-Schottky plots indicate n-type behavior for ZnO and $(Zn_{1-x}Co_x)O$ NWs. Considering value of ϵ to be 10, the carrier density of ZnO NWs is calculated to be $2.35 \times 10^{18} \text{ cm}^{-3}$ at the frequency of 7.5 kHz (**Section S2 and Table 2**), which is almost similar to the typical value of 10^{17} - 10^{18} cm^{-3} observed for ZnO NWs reported in the literature.[27] The carrier density for $(Zn_{0.95}Co_{0.05})O$ and $(Zn_{0.9}Co_{0.1})O$ NWs are $3.98 \times 10^{18} \text{ cm}^{-3}$ and $5.02 \times 10^{18} \text{ cm}^{-3}$, respectively (**Table 2**). This shows that the increase in Co concentration in ZnO NWs leads to increase in carrier density, in comparison to undoped ZnO NWs. This increment in carrier density is thus important as it offers more photogenerated electrons available for the photoelectrochemical (PEC) water splitting reaction.

Photoelectrochemical (PEC) characterization of $(Zn_{1-x}Co_x)O$ NWs ($x=0, 0.05, 0.1$)

The photoelectrochemical (PEC) activity of undoped ZnO and $(Zn_{1-x}Co_x)O$ NWs was studied in 0.5 M Na_2SO_4 aqueous electrolyte solution (with pH buffered to ~ 7.0). **Fig. 3a** shows the linear scan voltammogram (LSV) curves for ZnO and $(Zn_{1-x}Co_x)O$ NWs, in the dark and under illumination of 100 mW cm^{-2} obtained with a scan rate of 1 mV sec^{-1} . Dark scan LSV curves showed a small current density in the range of $10^{-3} \text{ mA cm}^{-2}$ for ZnO and $(Zn_{1-x}Co_x)O$ NWs. Undoped ZnO NWs showed the onset potential of 0.28 V (vs RHE), similar to that reported earlier[30] and a photocurrent density of 0.032 mA cm^{-2} at 0.79 V (vs RHE), under illumination with light. In comparison to the undoped nanowires, $(Zn_{0.95}Co_{0.05})O$ and

297 (Zn_{0.9}Co_{0.1})O NWs demonstrate superior photoelectrochemical (PEC) activity with an onset
 298 potential of 0.15 V (*vs* RHE) and improved photocurrent density of 0.13 mA cm⁻² and 0.075 mA
 299 cm⁻² at 0.79V (*vs* RHE) in the *iR*_Ω corrected LSV plot, respectively, as shown in **Fig. 3a and**
 300 **Table 2**. Thus, (Zn_{0.95}Co_{0.05})O shows ~306% and ~134% improved photocurrent density
 301 compared to that of ZnO and (Zn_{0.9}Co_{0.1})O NWs. The improved photocurrent density after Co
 302 doping in ZnO can be attributed to the improved light absorption (**Fig. 1 (a-b)**) and increased
 303 carrier density, as observed from the Mott-Schottky analysis (**Fig. 2 and Table 2**). It is expected
 304 that (Zn_{0.9}Co_{0.1})O NWs will likely exhibit higher photocurrent density than (Zn_{0.95}Co_{0.05})O NWs
 305 due to its lower band gap, improved light absorption, as seen in the UV-vis absorption spectra
 306 and Tauc analysis in **Fig. 1 (a-b)** and increase in the number of carriers, as deduced from the
 307 Mott-Schottky analysis (**Fig. 2**) than (Zn_{0.95}Co_{0.05})O NWs. However, the higher photocurrent
 308 density exhibited by (Zn_{0.95}Co_{0.05})O NWs contrasted with (Zn_{0.9}Co_{0.1})O NWs shows the
 309 improved reaction kinetics displayed by (Zn_{0.95}Co_{0.05})O NWs compared to (Zn_{0.9}Co_{0.1})O NWs.
 310 Hence, electrochemical impedance spectroscopy (EIS) has been carried out to study the reaction
 311 kinetics (**Fig. 6d**). The low frequency EIS plots of ZnO and (Zn_{1-x}Co_x)O (*x*=0.05, 0.1) NWs,
 312 shown in **Fig. 6d**, displays the well-formed semicircle, which can be related to water oxidation
 313 reaction. The diameter of the low frequency semicircle which relates to the polarization
 314 resistance (*R*_{ct}) and thus, the photoelectrochemical (PEC) activity of the semiconductor material
 315 of (Zn_{0.95}Co_{0.05})O NWs (70 Ω.cm²) is lower than (Zn_{0.9}Co_{0.1})O NWs (80.8 Ω.cm²) and pure ZnO
 316 NWs (90 Ω.cm²) (**Table 3**). This indicates the improved reaction kinetics for (Zn_{0.95}Co_{0.05})O
 317 NWs than (Zn_{0.9}Co_{0.1})O NWs, suggesting relatively efficient separation and thus, reduced
 318 recombination of photogenerated carriers resulting in higher photocurrent density for
 319 (Zn_{0.95}Co_{0.05})O NWs than (Zn_{0.9}Co_{0.1})O NWs.[66, 67]

The solar to hydrogen efficiency (SHE) for ZnO and (Zn_{1-x}Co_x)O NWs is calculated using the equation[30, 68]:

$$\text{SHE} = I(1.23 - V) \times 100 / J_{\text{light}} \dots \dots \dots (1)$$

where, I is the photocurrent density at the measured potential, V is the applied potential and J_{light} is the illumination intensity of 100 mW cm⁻². The variation in SHE with applied potential is shown in **Fig. 3b**. (Zn_{0.95}Co_{0.05})O NWs exhibited higher SHE (0.058% at 0.82V *vs* RHE) than ZnO (0.016% at 0.92V *vs* RHE) and (Zn_{0.9}Co_{0.1})O NWs (0.034% at 0.82V *vs* RHE), respectively. The lower SHE for (Zn_{0.9}Co_{0.1})O NWs contrasted with (Zn_{0.95}Co_{0.05})O NWs can mainly be attributed to improved reaction kinetics for (Zn_{0.95}Co_{0.05})O NWs compared to (Zn_{0.9}Co_{0.1})O NWs, as seen in EIS analysis (**Fig. 6d and Table 3**). Hence, in the present study, 5% cobalt doped ZnO NWs have been selected to study the doped compositions on account of their photoelectrochemical performance being significantly better than the undoped ZnO NWs and 10% cobalt doped ZnO NWs. Although (Zn_{0.95}Co_{0.05})O NWs exhibit improved photoelectrochemical response as photoanode than ZnO and (Zn_{0.9}Co_{0.1})O NWs, the SHE achieved for (Zn_{0.95}Co_{0.05})O NWs is still poor, in the context of what is desired for potential commercialization of PEC water splitting system for hydrogen generation.[48, 49] Hence, it is important to improve the photoelectrochemical (PEC) performance of (Zn_{0.95}Co_{0.05})O NWs further, which can be achieved by lowering the band gap of (Zn_{0.95}Co_{0.05})O NWs even further, which will offer improved light absorption and increase in the number of photogenerated carriers available for reaction. This is achieved by following a co-doping strategy, using nitrogen as a likely and potential dopant for (Zn_{0.95}Co_{0.05})O NWs.

3.2 Synthesis and characterization of (Zn_{1-x}Co_x)O:N NWs (x=0.05)

N doping has been accordingly carried out by the heat treatment of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs at different temperatures (400°C , 500°C , 600°C and 700°C) in anhydrous NH_3 atmosphere. Experimental study has been conducted at different temperatures of heat treatment in NH_3 atmosphere to study the role of nitrogen in the modification of the electronic structure of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs and thus, better correlate the optical and photoelectrochemical (PEC) properties with different concentration of nitrogen doped in the lattice of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs.[60, 61] Accordingly, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs, heat treated in NH_3 at 400°C is denoted as $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$ NWs in this study. Similarly, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs, heat treated in NH_3 at 500°C , 600°C and 700°C are systematically denoted as $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$ NWs, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-700}$ NWs, respectively. The structural characterization of $(\text{Zn}_{1-x}\text{Co}_x)\text{O:N}$ NWs is discussed in **Section S2**.

UV-vis absorption and Tauc analysis of $(\text{Zn}_{1-x}\text{Co}_x)\text{O:N}$ NWs ($x=0.05$)

The optical properties of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs are studied using UV-vis absorption spectroscopy. UV-vis absorption spectra of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$ and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs are shown in **Fig. 4a**, along with ZnO and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs for comparison. $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs show excellent light absorption behavior in the visible region of interest, in comparison to pure ZnO and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs. The absorption peaks for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs for different N concentration are red-shifted to higher wavelengths compared to ZnO and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs and the red-shift increases with increase in N concentration. $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$ and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs show $\sim 117\%$, $\sim 483\%$, $\sim 598\%$ and $\sim 30\%$, $\sim 250\%$, $\sim 317\%$ improved light absorption at 500 nm, in comparison to pure ZnO and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs, respectively. The corresponding Tauc

analysis, shown in **Fig. 4b**, was carried out for estimation of the band gap of (Zn_{0.95}Co_{0.05})O:N-400, (Zn_{0.95}Co_{0.05})O:N-500 and (Zn_{0.95}Co_{0.05})O:N-600 NWs. The values of band gap are determined from the x-intercept of $(\alpha h\nu)^2$ vs $h\nu$ curves. As shown in **Fig. 4b** and **Table 2**, reduction in band gap with increase in N concentration is seen for (Zn_{0.95}Co_{0.05})O:N NWs, with the lowest band gap obtained for (Zn_{0.95}Co_{0.05})O:N-600 NWs (2.16 eV). It is noteworthy that Co and N co-doping helped in significantly reducing the band gap of ZnO from 3.18 eV to 2.16 eV for (Zn_{0.95}Co_{0.05})O:N-600 NWs (**Table 2**). The reduction in the band gap is important since it offers improved light absorption and thus, an improved photoelectrochemical (PEC) performance due to increase in the number of photogenerated carriers available for the reaction.

Mott-Schottky analysis of (Zn_{1-x}Co_x)O:N NWs (x=0.05)

The electronic properties of (Zn_{0.95}Co_{0.05})O:N NWs were studied by Mott-Schottky analysis, carried out using EIS performed in the dark, shown in **Fig. 5**. The flat band potential (V_{FB}) of (Zn_{0.95}Co_{0.05})O:N-400 NWs, (Zn_{0.95}Co_{0.05})O:N-500 NWs and (Zn_{0.95}Co_{0.05})O:N-600 NWs, determined from the x-intercept in Mott-Schottky plots ($1/C^2$ vs V), are $\sim(-0.58$ V vs NHE), $\sim(-0.59$ V vs NHE) and $\sim(-0.66$ V vs NHE), respectively. The values of V_{FB} of (Zn_{0.95}Co_{0.05})O:N NWs of different N concentration are more negative (cathodic) than the calculated V_{FB} of -0.413V (vs NHE) (**Section S2**) suggesting that band edges of (Zn_{0.95}Co_{0.05})O:N NWs are more negative than the reduction potential of water. Additionally, n-type behavior is seen for (Zn_{0.95}Co_{0.05})O:N NWs, as evidenced by the positive slope obtained in Mott-Schottky plot. The carrier density of (Zn_{0.95}Co_{0.05})O:N-400, (Zn_{0.95}Co_{0.05})O:N-500 and (Zn_{0.95}Co_{0.05})O:N-600 NWs is 3.1×10^{22} cm⁻³, 3.98×10^{22} cm⁻³ and 4.66×10^{22} cm⁻³ at frequency of 7.5 kHz, which is 4-orders of magnitude higher than the carrier density determined for

(Zn_{0.95}Co_{0.05})O NWs (3.98×10¹⁸ cm⁻³) and pure ZnO NWs (2.35×10¹⁸ cm⁻³) (**Table 2**). The carrier density of 4.66×10²² cm⁻³ of (Zn_{0.95}Co_{0.05})O:N-600 NWs is the highest carrier density obtained for ZnO based nanostructured photoanodes reported so far, which clearly suggests the profound influence of Co and N co-doping leading to significant improvement in the carrier density of ZnO NWs.[27, 31, 69] The increased carrier density is expected to shift the Fermi level upwards towards the conduction band, which will distinctly help in achieving improved charge separation at the interface between the (Zn_{0.95}Co_{0.05})O:N NWs and the electrolyte solution, due to an increased degree of band bending.[70, 71] The improved band bending for (Zn_{0.95}Co_{0.05})O:N NWs is expected to offer large driving force for the photogenerated electrons resulting in improved photocurrent density and thus, expectedly an improved photoelectrochemical (PEC) performance, compared to pure ZnO and (Zn_{0.95}Co_{0.05})O NWs.

IPCE of (Zn_{1-x}Co_x)O:N NWs (x=0.05):

The incident photon to current efficiency (IPCE) was studied using different band pass optical filters to correlate the optical properties with photoelectrochemical properties for the synthesized co-doped (Zn_{0.95}Co_{0.05})O:N-400, (Zn_{0.95}Co_{0.05})O:N-500 and (Zn_{0.95}Co_{0.05})O:N-600 NWs. The IPCE values for (Zn_{0.95}Co_{0.05})O:N-400, (Zn_{0.95}Co_{0.05})O:N-500 and (Zn_{0.95}Co_{0.05})O:N-600 NWs are obtained by measuring the photocurrent density upon light illumination using different band pass optical filters with wavelengths centered at 350, 400, 450, 500, 550 and 600 nm, shown in **Fig. 6a**. The corresponding IPCE is calculated by the equation[72]:

$$IPCE (\%) = \frac{1240 \lambda J \times 100}{h \nu P}$$

where, J is the measured photocurrent density (mA cm⁻²), P is the incident light intensity (mW cm⁻²) at a specific wavelength (λ, nm). An increase in IPCE is observed with increase in N

concentration for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs, which can be attributed to decrease in band gap and significant increase in carrier density which offers enhanced charge separation and improved charge transport (which is confirmed by EIS analysis discussed later) in $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs due to superior band bending as discussed earlier. The corresponding IPCE at the wavelength of 500 nm for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$ and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs are 1.9%, 3.5% and 15%, respectively. It is noteworthy that the IPCE of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs is significantly higher than that of pure ZnO NWs ($\sim 0\%$ at 500 nm), suggesting the beneficial role of Co and N co-doping in not only lowering the band gap and offering improved light absorption, but also improved charge collection and conversion efficiency in the visible region of interest.[27] The IPCE for undoped ZnO nanowires (NWs) is 2.5% at 350 nm (which is in UV region) (**Fig. 6a**) which is similar to that obtained earlier.[73, 74] The poor IPCE of ZnO NWs under UV light is mainly due to (I) low carrier density (**Table 2**), (II) high charge transfer resistance (R_{ct} , discussed later) leading to poor carrier mobility and superior recombination of photogenerated carriers (**Fig. 6d** and **Table 3**). The highest IPCE obtained in this study obtained for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs (15% at 500 nm) is the highest IPCE reported so far for ZnO based photoanodes, to the best our knowledge.[27, 30, 31, 35, 47, 69, 75] This shows that Co and N co-doping is indeed a promising strategy for improving photoelectrochemical response of ZnO.

Photoelectrochemical characterization of $(\text{Zn}_{1-x}\text{Co}_x)\text{O:N}$ NWs ($x=0.05$)

The photoelectrochemical activity of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs is studied using 0.5 M Na_2SO_4 aqueous solution (with pH buffered to ~ 7.0) as the electrolyte. **Fig. 6b** shows LSV curves for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$ and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs, in the

435 dark and with illumination of 100 mW cm^{-2} , obtained with a scan rate of 1 mV sec^{-1} . Dark scan
 436 LSV curves showed a small current density in the range of $\sim 10^{-3} \text{ mA cm}^{-2}$ for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$
 437 NWs. Under illumination, pronounced photocurrent density is seen for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs,
 438 which increases with increase in potential. The onset of photocurrent density under illumination
 439 starts at (-0.02 V vs RHE) for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$ and
 440 $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs, respectively (**Table 2**). Thus, the lower onset potential of
 441 $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs than that of ZnO (0.28 V), $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ (0.15 V) (**Table 2**) suggests
 442 improvement in photoelectrochemical activity upon N doping in $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs. The onset
 443 potential of (-0.02 V) obtained for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$ NWs, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$ NWs and
 444 $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs in this study is the lowest onset potential obtained for ZnO based
 445 photoanode materials studied so far as shown in **Table 1** suggesting excellent
 446 photoelectrochemical activity of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs than other ZnO based materials studied
 447 so far. The photocurrent density at 0.79 V (vs RHE) in iR_{Ω} corrected LSV plots for
 448 $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$ and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs is 3.56 mA cm^{-2} ,
 449 6.56 mA cm^{-2} and 8.78 mA cm^{-2} , respectively (**Table 2**). This shows that the
 450 photoelectrochemical activity increases with increase in N concentration for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$
 451 NWs. The maximum photocurrent density obtained for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs (8.78 mA
 452 cm^{-2}) is $\sim 147\%$ and $\sim 34\%$ higher than that of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$ (3.56 mA cm^{-2}) and
 453 $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$ NWs (6.56 mA cm^{-2}), respectively. It is also noteworthy that the
 454 photocurrent density of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs (8.78 mA cm^{-2}) is ~ 68 and ~ 275 times
 455 higher than that of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs (0.13 mA cm^{-2}) and ZnO NWs (0.032 mA cm^{-2}). The
 456 excellent photoelectrochemical activity of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs can be attributed to
 457 significantly reduced band gap (**Fig. 4 b and Table 2**) resulting in superior light absorption (**Fig.**

4a), high carrier density (**Fig. 5 and Table 2**), improved charge separation and collection (**Fig. 6a**) and improved electron transfer (shown by EIS analysis under illumination discussed later) at the interface between the (Zn_{0.95}Co_{0.05})O:N NWs and electrolyte solution.

The variation of solar to hydrogen efficiency (SHE), calculated using **Eqn. 1** with the applied potential is shown in **Fig. 6c**. The maximum SHE, observed for (Zn_{0.95}Co_{0.05})O:N-400, (Zn_{0.95}Co_{0.05})O:N-500 and (Zn_{0.95}Co_{0.05})O:N-600 NWs, is 0.82%, 0.92% and 1.39% at 0.79V (*vs* RHE), which is ~51, ~57, ~87 fold and ~14, ~16, ~24 fold higher than that of ZnO (0.016% at 0.92 V *vs* RHE) and (Zn_{0.95}Co_{0.05})O NWs (0.058% at 0.82 V *vs* RHE), respectively (**Table 2**). The superior SHE obtained at low potential for (Zn_{0.95}Co_{0.05})O:N NWs shows the beneficial role of N as potential dopant in improving the SHE of (Zn_{0.95}Co_{0.05})O NWs. The maximum SHE for (Zn_{0.95}Co_{0.05})O:N-600 NWs (1.39%) is ~70% and ~51% higher than that of (Zn_{0.95}Co_{0.05})O:N-400 (0.82%) and (Zn_{0.95}Co_{0.05})O:N-500 NWs (0.92%), respectively. To the best of our knowledge and based on values of SHE for different ZnO materials studied so far given in **Table 1**, the SHE of 1.39% for (Zn_{0.95}Co_{0.05})O:N-600 NWs is the maximum SHE, reported thus far, at considerably lower potential (0.79 V *vs* RHE) than the other ZnO based materials. These results thus suggest the remarkable improvement in photoelectrochemical activity of ZnO by Co and N co-doping.

Table 1: Efficiency of photoelectrochemical water splitting of various ZnO photoanode materials, reported in the literature

No.	Photoanode material	Max. SHE,	Potential at max.	Onset potential	Ref

		%	SHE (V, RHE)	(V, RHE)	
1	N-doped ZnO nanowire arrays	0.15	1.11	0.21	[27]
2	N-doped ZnO nanotetrapods	0.31	0.92	0.41	[69]
3	ZnO:Al nanorod array thin film	0.02	0.5 (vs Ag/AgCl)	0.61	[76]
4	Bent ZnO nanorod photoanode	0.08	0.69	-	[77]
5	Si/ZnO core/shell nanowire arrays	0.38	0.65 (vs Ag/AgCl)	0.11	[78]
6	Hierarchical ZnO/WO _x nanowires	0.2	0.25	0.01	[79]
7	C-doped ZnO porous nanoarchitectures	0.75	0.91	0.31	[47]
8	Si/ZnO core/shell nanowire arrays	0.035	1.15	0.36	[80]
9	ZnO:Cu nanostructured film	0.28	0.6 (vs Ag/AgCl)	1.44	[35]
10	ZnFe ₂ O ₄ /ZnO system	0.15	1.21	0.51	[75]

11	ZnO-ZnS core-shell	0.38	0.81	0.26	[31]
12	Au coated 3D ZnO nanowires	0.52	0.75	0.3	[30]
13	<u>(Zn_{0.95}Co_{0.05})O:N-600 NWs</u>	<u>1.39</u>	<u>0.79</u>	<u>-0.02</u>	<u>Present work</u>

Electrochemical impedance spectroscopy of (Zn_{1-x}Co_x)O:N NWs (x=0.05) under illumination:

In addition to the optoelectronic and photoelectrochemical properties discussed above, electron transfer properties are also of considerable importance in understanding the photoelectrochemical processes operational for the facile hydrogen production from PEC water splitting. Higher SHE obtained for (Zn_{0.95}Co_{0.05})O:N-600 NWs compared to (Zn_{0.95}Co_{0.05})O:N-400 and (Zn_{0.95}Co_{0.05})O:N-500 NWs could possibility indicate improved electrochemical reaction kinetics in addition to increased light absorption (**Fig. 4 (a-b)**), carrier density (**Fig. 5** and **Table 2**) and charge collection and conversion efficiency or IPCE (**Fig. 6a**) for (Zn_{0.95}Co_{0.05})O:N-600 NWs than (Zn_{0.95}Co_{0.05})O:N-400 and (Zn_{0.95}Co_{0.05})O:N-500 NWs. Hence, to understand the reaction kinetics for (Zn_{0.95}Co_{0.05})O:N NWs, electrochemical impedance spectroscopy (EIS) was carried out to study the charge transfer resistance (R_{ct}) at the photoelectro-catalyst/electrolyte interface. R_{ct} for (Zn_{0.95}Co_{0.05})O:N NWs decreases with increase in N concentration with the lowest R_{ct} for (Zn_{0.95}Co_{0.05})O:N-600 NWs (16 $\Omega \cdot \text{cm}^2$), indicating the improved reaction kinetics for (Zn_{0.95}Co_{0.05})O:N NWs with increase in N concentration (**Fig. 6d** and **Table 3**). Also, it should be noted that the R_{ct} for (Zn_{0.95}Co_{0.05})O:N-600 NWs (16 $\Omega \cdot \text{cm}^2$) is almost six-fold lower than pure ZnO (90 $\Omega \cdot \text{cm}^2$) and five-fold lower than (Zn_{0.95}Co_{0.05})O NWs (70 $\Omega \cdot \text{cm}^2$) and (Zn_{0.9}Co_{0.1})O NWs (80.8 $\Omega \cdot \text{cm}^2$). These results thus show that the

electrochemical reaction kinetics and thus, photoelectrochemical activity is superior for (Zn_{0.95}Co_{0.05})O:N-600 NWs, in comparison to ZnO NWs, (Zn_{0.95}Co_{0.05})O NWs, (Zn_{0.9}Co_{0.1})O NWs, (Zn_{0.95}Co_{0.05})O:N-400 NWs and (Zn_{0.95}Co_{0.05})O:N-500 NWs, which compounded together aid in achieving the maximum SHE of 1.39% for (Zn_{0.95}Co_{0.05})O:N-600 NWs. The lower R_{ct} for (Zn_{0.95}Co_{0.05})O:N-600 NWs could possibly be attributed to the efficient separation and thus, minimum recombination of the photogenerated carriers, as seen in IPCE analysis (**Fig. 6a**).[66, 67] The facile nature of the reaction kinetics in addition to improved optoelectronic characteristics renders (Zn_{0.95}Co_{0.05})O:N-600 NWs a very promising material in comparison to other semiconductor materials hitherto under study.

Photoelectrochemical stability of (Zn_{1-x}Co_x)O:N NWs (x=0.05)

The photoelectrochemical (PEC) stability of semiconductor material (photoanode) is important for long term operation of PEC water splitting system for hydrogen generation. Hence, to study the photoelectrochemical stability of (Zn_{0.95}Co_{0.05})O:N-600 NWs, chronoamperometry (CA) test is carried out at 0.79 V (*vs* RHE) (at which max. SHE of 1.39% is obtained for (Zn_{0.95}Co_{0.05})O:N-600 NWs) under illumination for 24 h in the 0.5 M Na₂SO₄ electrolyte solution (with pH buffered to ~7.0). The CA curve for (Zn_{0.95}Co_{0.05})O:N-600 NWs is shown in **Fig. 7a**. The very minimal loss in photocurrent density is seen for (Zn_{0.95}Co_{0.05})O:N-600 NWs indicating excellent photoelectrochemical stability of (Zn_{0.95}Co_{0.05})O:N-600 NWs. Also following the 24 h CA test, LSV is carried out to ensure that (Zn_{0.95}Co_{0.05})O:N-600 NWs displays no degradation and is exhibiting similar photoelectrochemical activity, prior to the start of the CA test. The LSV curve after 24 h CA test shown in **Fig. 7b**, indeed shows negligible loss in photoelectrochemical activity for (Zn_{0.95}Co_{0.05})O:N-600 NWs. ICP analysis conducted on the electrolyte solution,

collected after the CA test does not show the presence of Zn and Co for (Zn_{0.95}Co_{0.05})O:N-600 NWs. To compare the photoelectrochemical stability of (Zn_{0.95}Co_{0.05})O:N-600 NWs with ZnO NWs, CA test is also carried out for pure ZnO NWs under similar conditions as that used for (Zn_{0.95}Co_{0.05})O:N-600 NWs. The CA curve for pure ZnO (**Fig. 7c**) shows steady drop in photocurrent density, indicating poor photoelectrochemical stability of ZnO NWs. These results clearly show the superior photoelectrochemical (PEC) stability of (Zn_{0.95}Co_{0.05})O:N-600 NWs under illumination in the electrolyte 0.5 M Na₂SO₄ (pH 7) electrolyte solution over extended period of time compared to that of pure ZnO NWs. ZnO is known to undergo photocorrosion [81] resulting in the fade behavior as observed in **Fig. 7c**. The gradual deactivation of ZnO occurs as a result of production of electron-hole pairs in the presence of light wherein the electrons are separated to the cathode where they react with H⁺ ions to generate hydrogen gas. The holes on the other hand, on the surface of ZnO oxidize water to generate oxygen gas. Two factors play a role in photo-corrosion of ZnO-(a) rate of electron-hole generation (b) rate of electrochemical consumption of holes by the reaction[82]:

In the event that the rate of the electrochemical reaction is very sluggish, an excess of holes is created on the ZnO surface resulting in photocorrosion by reaction[81]:

This is the case with the undoped ZnO NWs observed in this study. The six-fold lower R_{ct} than ZnO NWs (**Fig. 6d** and **Table 3**) along with significantly higher IPCE for (Zn_{0.95}Co_{0.05})O:N-600 NWs (**Fig. 6a**) indicates far more expeditious carrier generation, transport and conversion for (Zn_{0.95}Co_{0.05})O:N-600 NWs than undoped ZnO NWs due to increased carrier density (offered by

Co and N co-doping) resulting in improved band bending at the semiconductor-electrolyte interface (as discussed earlier). Thus, this suggests that photogenerated carriers are rapidly consumed in the water oxidation process for (Zn_{0.95}Co_{0.05})O:N-600 NWs due to superior reaction kinetics (**Fig. 6d** and **Table 3**) offered by Co and N co-doping, compared to that for the undoped ZnO NWs. In addition, ICP analysis of electrolyte solution collected after the CA test does not show the presence of Zn and Co for (Zn_{0.95}Co_{0.05})O:N-600 NWs. Thus, the deactivation process of the semiconductor material by holes is minimal for doped ZnO, .i.e., (Zn_{0.95}Co_{0.05})O:N-600 NWs resulting in superior long term photoelectrochemical stability as seen in the CA curve and minimal loss in photoelectrochemical activity after 24 h of CA test conducted under illumination (**Fig. 7a-b**). However, significantly higher R_{ct} (**Fig. 6d** and **Table 3**) values observed for undoped ZnO NWs indicates poor water oxidation reaction kinetics. Hence, excess holes can possibly deactivate ZnO NWs (by reaction mentioned above) resulting in a steady drop in the photocurrent density as seen in the CA curve (**Fig. 7c**).

Measurement of H₂ and O₂ gases under illumination:

It is important to measure the concentration of H₂ and O₂ gases generated at the cathode and photoanode, respectively, to ensure that the photocurrent density is arising from the water splitting reaction and that no current density is resulting from any adventitious unwanted side reactions. Hence, during the CA test of (Zn_{0.95}Co_{0.05})O:N-600 NWs at constant potential of 0.79 V (vs RHE), the concentration of gases evolved was measured at 1 h intervals by gas chromatography (helium used as the carrier gas). Also, the theoretical concentration of H₂ gas is calculated from the measured photocurrent density using the Faraday's law given as:[72]

$$\text{No. of moles of H}_2 = \frac{Q}{2F} = \frac{It}{2F} = \frac{\int_0^t i dt}{2F}$$

where, I is the photocurrent density, t is time, F is the Faraday constant (96484.34 C/mole) and Q is the quantity of charge in coulomb. The concentration of theoretical and experimentally measured H_2 gas and O_2 gases measured during the CA test for $(Zn_{0.95}Co_{0.05})O:N-600$ NWs are shown in **Fig. 7d**. The measured amount of evolved H_2 gas is closer or comparable to the theoretical amount of H_2 indicating ~100% Faradaic efficiency for hydrogen generation. In addition, the ratio of concentration of generated H_2 and O_2 gases is ~2 and also, no change is observed in the pH of the electrolyte solution (~7) before and after water splitting reaction, suggesting that there is stoichiometric decomposition of water to H_2 and O_2 occurring in the present study for $(Zn_{0.95}Co_{0.05})O:N-600$ NWs. These results therefore show the excellent long term photoelectrochemical stability of $(Zn_{0.95}Co_{0.05})O:N-600$ NWs for hydrogen generation under illumination, which is of paramount importance for the potential commercialization of the PEC water splitting cell system.

3.3 Results of the computational study

Pure ZnO

It should be noted that there are several published theoretical studies dedicated to pure and doped ZnO and the electronic structure of the oxide has already been thoroughly discussed in the literature (see, for example,[83-85]). However, in the context of the current study it is logical and pertinent to describe the electronic structure of ZnO. In addition, pure ZnO will be used to illustrate the combined Co- and N-doping effects on the ZnO electronic structure.

The total and projected densities of electronic states calculated for pure ZnO are shown in **Fig. 8a**. The primary energy band structure of ZnO consists of three bands. The low energy band between -17 and -18 eV is composed of the 2s states of oxygen. The wide valence band within

the energy interval from -6.1 to 0.0 eV consists of Zn 3d states located primarily between -6.1 and -4 eV and O 2p states located between -4 eV and the Fermi level. Finally, the conduction band consists mainly of hybridized Zn 4s and O 2p electronic states separated from the valence band by the energy gap E_{bg} of 0.89 eV. This value of the forbidden gap is underestimated substantially in comparison to the experimental value of 3.18 eV as seen in **Table 4** [86], which is the well-known intrinsic characteristic limitation of DFT calculations arising from the self-interaction effects and derivative discontinuities of the exchange correlation energy. However, for the purposes of the present study, a precise calculation of the band gap is not essentially critical since the goal of the present work is to assess the overall effect of Co and N co-doping on the electronic structure of ZnO and hence general trends of the electronic structure modifications during doping of ZnO is deemed sufficient. Hence, this disadvantage of DFT will not affect the results obtained and discussed in the current manuscript. Furthermore, the main parameters of the electronic structure for ZnO calculated in the present study do agree well with the results obtained from previously published theoretical calculations.[83, 84, 87]

ZnO doped with Co and N

Calculated total and projected densities of the electronic states for $(\text{Zn}_{0.9375}\text{Co}_{0.0625})\text{O}$ oxide composition are shown on **Fig. 8b**. It can be seen that the main band structure of the Co-doped ZnO is similar to the undoped oxide. However, the main difference between the two is the appearance of the Co-3d electronic states within the Fermi level vicinity. A narrow Co-3d spin-up states located at the top of the valence band are strongly hybridized with O-2p electrons and separated from almost non-hybridized conduction Co-3d spin-down states by the energy gap of 0.45 eV. This optical band gap value is noticeably smaller than the E_{BG} calculated for the pure

ZnO (0.89 eV) which agrees well with experimental observations (**Table 4**) demonstrating narrowing of the optical band gap following Co-doping of ZnO. Of course, both values are significantly underestimated due to the reasons discussed above. However the relative difference between these values is qualitatively the same as that observed experimentally. It should also be noted that since the impurity Co-3d states locate at the Fermi level, it clearly indicates that Co doped ZnO is n-type semiconductor, which is also experimentally verified from the Mott-Schottky analysis (**Fig. 2**). Additionally, the calculated electronic structure is very similar to other spin-polarized calculations reported in the literature[88].

To further elucidate the effects of nitrogen doping on the electronic structure of ZnO, $(\text{ZnO}_{0.9375})\text{:N}_{0.0625}$ has been considered as a representative composition. The projected density of electronic states for this composition is shown in **Fig. 8c**. As described above, it can be seen that the general picture is almost identical to that for pure ZnO. The only difference between pure and N-doped ZnO oxide is the appearance of N-2p impurity states at the top of the valence band. The calculated band gap E_{BG} is 0.7 eV which is noticeably narrower than the corresponding band gap of 0.89 eV for pure ZnO. This trend also agrees well with calculations reported by Xu. Zong *et al.*[89]. Thus, the addition of N can helps in decreasing the optical band gap further and extend the absorption of ZnO to the visible region.

Simultaneous co-doping of nitrogen together with cobalt into ZnO significantly influences the electronic structure of the system within the Fermi level vicinity. **Fig. 8 (d-e)** show the calculated projected density of electronic states for $(\text{Zn}_{0.9375}\text{Co}_{0.0625})\text{O}_{0.9375}\text{:N}_{0.0625}$ and $(\text{Zn}_{0.9375}\text{Co}_{0.0625})\text{O}_{0.875}\text{:N}_{0.125}$ respectively. From **Fig. 8d**, it can be seen that there is a new impurity band originated from N-2p states located right in place of the optical band gap presented in Co-doped ZnO (see **Fig. 8b**). Being strongly hybridized with spin-down Co-3d

states, this band closes completely the former optical band gap located below the Fermi level of Co-doped ZnO. However, new optical band gap opens above the Fermi level separating the spin-down filled and empty Co-3d states. Calculated value of this band gap is 0.34 eV. An increase in the N-content in the compound results in further narrowing of the optical band gap up to 0.23 eV as shown on **Fig. 8e**. Otherwise, the overall electronic structure for 12.5 at% N remains identical to that of the previous case for 6.25 at% of N. Thus, the present computational study provides a qualitative agreement and validation of the experimental observations reflecting a general trend of narrowing the optical band gap obtained by Co and N co-doping of ZnO. The calculated and experimentally measured optical band gaps for all the materials considered in the present study are shown in **Table 4**.

The present experimental and theoretical study thus demonstrates the excellent photoelectrochemical (PEC) performance and stability of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs with solar to hydrogen efficiency (SHE) of 1.39%, which is the maximum SHE achieved so far for ZnO based photoanode materials (**Table 1**). This remarkable improvement in photoelectrochemical (PEC) performance of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs as compared to pure ZnO NWs can be attributed to improved light absorption properties of doped ZnO leading to the reduction in the band gap of pure ZnO NWs from 3.18 eV to 2.16 eV for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs resulting in improved light absorption (**Fig. 4 a-b**), the concurrent improvement in electronic properties i.e. improved carrier density (**Fig. 5 and Table 2**), improved carrier transport and collection efficiency (**Fig. 6a**) and improved electrochemical charge transfer (**Fig. 6d and Table 2**) further contribute to the observed excellent photoelectrochemical activity of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs, compared to the other materials considered in this study. The excellent photoelectrochemical stability of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs is evidenced by the long term CA

test carried out under illumination for 24 h (**Fig. 7a**). The above results also clearly show that (Zn_{0.95}Co_{0.05})O:N-600 NWs is indeed promising semiconductor material with excellent photoelectrochemical performance and stability and promising SHE of 1.39%. The study conducted thus opens up new ground for exploring the different ZnO based materials as photoanode for PEC water splitting on the grounds of remarkable visible light absorption characteristics and photoelectrochemical stability exhibited by (Zn_{0.95}Co_{0.05})O:N-600 NWs for possibly long term operation and extended use. The study conducted and reported herein is extremely important and demonstrates a pathway for gradually transitioning towards efficient hydrogen generation by utilizing solar energy in an environmentally benign fashion and thus, potentially solving the colossal global energy demand arising due to the ever-increasing global population and concomitant need for energy.

4. Conclusion

The present study explores (Zn_{1-x}Co_x)O:N NWs (x=0.05) as a potential photoanode for photoelectrochemical (PEC) water splitting. The nanowires were grown on FTO slide by a simple hydrothermal route, followed by heat treatment in NH₃ atmosphere. Our work has demonstrated cobalt and nitrogen as potential dopants for reducing the band gap of ZnO from 3.18 eV for pure ZnO NWs to 2.16 eV for (Zn_{0.95}Co_{0.05})O:N-600 NWs. The results of this study also establishes the effectiveness of co-doping using Co and N in ZnO NWs, which yields a four orders of magnitude improved carrier density, improved carrier separation, transport and collection efficiency, combined with superior photoelectrochemical activity with negative onset potential of (-0.02 V *vs* RHE), and excellent SHE. The optimal SHE of 1.39% obtained for (Zn_{0.95}Co_{0.05})O:N-600 NWs at 0.79V *vs* RHE (or 0.18 V *vs* Ag/AgCl) is the highest SHE

reported so far for ZnO nanostructured photoanodes. Additionally, long-term life test for 24 h showed excellent photoelectrochemical stability of (Zn_{0.95}Co_{0.05})O:N-600 NWs in the electrolyte solution under illumination, compared to pure ZnO NWs. Theoretical first principles calculations revealed strong effects of Co- and N-doping on electronic structure of ZnO in general and on the reduction of the optical band gap width in particular. This computational study has clearly demonstrated an ability of simultaneous doping of Co and N to decrease substantially the band gap and bring the absorption of ZnO into the visible region. The theoretical results agree well with the observed experimental results obtained in the present study. The co-doping strategy reported here has thus been seen to result in an improvement in photoelectrochemical performance through a conjunction of (a) improved light absorption (b) increased carrier density and (c) faster electrochemical charge transfer. Hence, it is envisaged that this work will be important in the search for semiconductor materials or photoanodes with high photoelectrochemical activity and stability in the electrolyte solution for long term operation, portending well with the overall aim of achieving efficient and economical hydrogen generation via water splitting by effective utilization of solar energy.

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Author contribution

P.P.P. and P.N.K. devised the original concept. P.P.P. designed the experiments, synthesized the materials, prepared the electrodes, performed the photoelectrochemical characterization and analyzed the photoelectrochemical data. O.I.V. conducted the theoretical analyses. J.P. and A.M. collected and analyzed the XPS data. P.P.P. performed SEM and EDAX. D. H. and B.G. carried out TEM and HRTEM. M.K.D. and P.J made important suggestions in the context of fundamental structural characterization and electrochemistry. P.P.P., O.I.V. and P.N.K. wrote the first draft of the paper; and all authors participated in the manuscript revision. The project is conceived and supervised by P.N.K.

Supporting information

Experimental details of structural characterization and photoelectrochemical study of all photoanode materials, details of computational methodology, Results of XRD study of pure ZnO NWs, $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0.05, 0.1$) and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs, SEM, EDAX, TEM, HRTEM study of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs, XPS study of ZnO and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs.

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Table 2: Results of Tauc analysis, Mott-Schottky analysis and photoelectrochemical characterization of ZnO, (Zn_{1-x}Co_x)O (x=0.05, 0.1) and (Zn_{0.95}Co_{0.05})O:N NWs of different N concentration, along with N concentration by EDAX

Composition	Band gap (eV)	Carrier density (cm ⁻³)	Onset potential (V, RHE)	Photocurrent density at 0.79V (RHE) (mA cm ⁻²)	Max. solar to hydrogen efficiency (SHE) (%)	Potential at max. SHE (V, RHE)	N concentration by EDAX (at. %)
ZnO	3.18	2.35×(10 ¹⁸)	0.28	0.032	0.016	0.92	-
(Zn _{0.95} Co _{0.05})O	2.98	3.98×(10 ¹⁸)	0.15	0.13	0.058	0.82	-
(Zn _{0.9} Co _{0.1})O	2.92	5.02×(10 ¹⁸)	0.15	0.075	0.034	0.82	-
(Zn _{0.95} Co _{0.05})O:N-400	2.49	3.1×(10 ²²)	-0.02	3.56	0.82	0.79	2.5
(Zn _{0.95} Co _{0.05})O:N-500	2.31	3.98×(10 ²²)	-0.02	6.56	0.92	0.79	6.4
(Zn _{0.95} Co _{0.05})O:N-600	2.16	4.6×(10 ²²)	-0.02	8.78	1.39	0.79	13.2

Table 3: Results of EIS analysis of ZnO, (Zn_{1-x}Co_x)O (x=0.05, 0.1) and (Zn_{0.95}Co_{0.05})O:N NWs of different N concentration, carried out at 0.79 V (vs RHE) in frequency range of 100 mHz-100 kHz (AC amplitude=10 mV) under illumination (100 mW cm⁻²) in 0.5 M Na₂SO₄ (pH 7) electrolyte solution

Composition	$R_s (\Omega\text{cm}^2)$	$R_e (\Omega\text{cm}^2)$	$R_{ct} (\Omega\text{cm}^2)$
ZnO	15.2	5.8	90
$(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$	15.22	5.74	70
$(\text{Zn}_{0.9}\text{Co}_{0.1})\text{O}$	15.2	5.71	80.8
$(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-400}$	15.21	5.7	25
$(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-500}$	15.2	5.65	20
$(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$	15.21	5.5	16

Table 4: Calculated and experimental optical band gaps E_{BG} for pure and doped ZnO

Composition	E_{BG} (eV) calc.	E_{BG} (eV) exp.
ZnO	0.89	3.18
$[\text{Zn}_{0.9375}\text{Co}_{0.0625}]\text{O}$	0.45	2.98
$\text{Zn}[\text{O}_{0.9375}\text{N}_{0.0625}]$	0.70	-
$[\text{Zn}_{0.9375}\text{Co}_{0.0625}][\text{O}_{0.9375}\text{N}_{0.0625}]$	0.34	2.31
$[\text{Zn}_{0.9375}\text{Co}_{0.0625}][\text{O}_{0.875}\text{N}_{0.125}]$	0.23	2.16

Figure captions:

877 **Figure 1:** (a) UV-vis absorption spectra of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$) (b) Tauc analysis
878 of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$).

879 **Figure 2:** Mott-Schottky plots of $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$) obtained by performing EIS
880 measurements in dark at a frequency of 7.5 kHz with an AC amplitude of 10 mV between
881 voltage window of -0.8 V to 1.2 V (vs NHE) in 0.5 M Na_2SO_4 (pH 7) electrolyte solution at
882 26°C.

883 **Figure 3:** (a) The linear scan voltammogram (LSV) curves for $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$)
884 in dark and illumination of 100 mW cm^{-2} in 0.5 M Na_2SO_4 (pH 7) electrolyte solution at 26°C,
885 before and after iR_Ω correction, (b) Solar to hydrogen efficiency (SHE) as a function of applied
886 potential for $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0, 0.05, 0.1$).

887 **Figure 4:** (a) UV-vis absorption spectra of ZnO, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ NWs and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$
888 NWs with different N contents (b) Tauc analysis of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs with different N
889 contents.

890 **Figure 5:** Mott-Schottky plot of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs of different N concentration obtained by
891 performing EIS measurements in dark at a frequency of 7.5 kHz with an AC amplitude of 10 mV
892 between voltage window of -0.8 V to 1.2 V (vs NHE) in 0.5 M Na_2SO_4 (pH 7) electrolyte
893 solution at 26°C.

894 **Figure 6:** (a) IPCE spectra of ZnO and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs of different N concentration, (b)
895 Linear scan voltammogram (LSV) curves for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs of different N
896 concentration in dark and illumination of 100 mW cm^{-2} measured in 0.5 M Na_2SO_4 (pH 7)
897 electrolyte solution at 26°C, before and after iR_Ω correction, (c) Solar to hydrogen efficiency
898 (SHE) as a function of applied potential for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs of different N concentration,

(d) EIS spectra of ZnO NWs, $(\text{Zn}_{1-x}\text{Co}_x)\text{O}$ NWs ($x=0.05, 0.1$) and $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N}$ NWs of different N concentration obtained at 0.79V (*vs* RHE) in 0.5 M Na_2SO_4 (pH 7) electrolyte solution at 26°C in the frequency range of 100 mHz to 100 kHz (AC amplitude=10 mV) under illumination (100 mW cm^{-2}), with the circuit used for fitting experimental data.

Figure 7: (a) The variation of photocurrent density *vs* time in the chronoamperometry test of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs, performed in a 0.5 M Na_2SO_4 (pH 7) electrolyte solution under a constant potential of 0.79V (*vs* RHE) at 26°C for 24 h (b) Linear scan voltammogram (LSV) curves for $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs in dark and illumination of 100 mW cm^{-2} measured in 0.5 M Na_2SO_4 (pH 7) electrolyte solution at 26°C, obtained after 24 h of chronoamperometry test, (c) The variation of photocurrent density *vs* time in the chronoamperometry test of ZnO NWs, performed in 0.5 M Na_2SO_4 (pH 7) electrolyte solution under a constant potential of 0.79V (*vs* RHE) at 26°C, (d) Theoretical and experimentally measured concentration of H_2 and O_2 gases, measured during chronoamperometry test of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O:N-600}$ NWs, performed in 0.5 M Na_2SO_4 (pH 7) electrolyte solution under a constant potential of 0.79V (*vs* RHE) at 26°C for 24 h.

Figure 8: (a) Projected density of states for pure ZnO. Fermi level is set for zero, (b) Total and projected density of states for ZnO doped with 6.25 at% of Co. Top panel is for spin-up, bottom panel is for spin-down. Fermi level is set for zero, (c) Projected density of states for ZnO doped with 6.25 at% of N. Fermi level is set for zero, (d) Projected density of states for ZnO doped with 6.25 at% of Co and 6.25 at% of N. Top panel is for spin-up, bottom panel is for spin-down. Fermi level is set for zero, (e) Projected density of states for ZnO doped with 6.25 at% of Co and 12.5 at% of N. Top panel is for spin-up, bottom panel is for spin-down. Fermi level is set for zero.

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Figure 1a

Figure 1b

Figure 2

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 5

Figure 6a

Figure 6b

Figure 6c

Figure 6d

Figure 7a

Figure 7b

Figure 7c

Figure 7d

Figure 8a

Figure 8b

Figure 8c

(d)

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Figure 8d

Figure 8e

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Table of contents entry

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