



Nitrogen and cobalt co-doped zinc oxide nanowires – Viable photoanodes for hydrogen generation via photoelectrochemical water splitting[☆]



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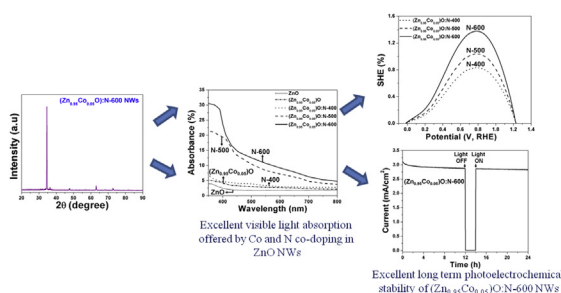
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HIGHLIGHTS

- Doping provides excellent optoelectronic properties for ZnO NWs.
- First principles study validates the optoelectronic properties of doped ZnO.
- $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}:\text{N}-600$ NWs exhibits superior SHE (1.39%) to date.
- Excellent photoelectrochemical stability of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}:\text{N}-600$ NWs.

GRAPHICAL ABSTRACT



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ABSTRACT

Photoelectrochemical (PEC) water splitting has been considered as a promising and environmentally benign approach for efficient and economic hydrogen generation by utilization of solar energy. Development of semiconductor materials with low band gap, high photoelectrochemical activity and stability has been of particular interest for a viable PEC water splitting system. In this study, Co doped ZnO, i.e., $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}$ nanowires (NWs) was selected as the composition for further 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 ($x = 0, 0.05, 0.1$). Furthermore, nanostructured vertically aligned Co and N-doped ZnO, i.e., $(\text{Zn}_{1-x}\text{Co}_x)\text{O}:\text{N}$ NWs ($x = 0.05$) have been studied as photoanodes for PEC water splitting. An optimal SHE of 1.39% the highest reported so far to the best of our knowledge for ZnO based photoanodes was obtained for the co-doped NWs, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}:\text{N}-600$ NWs generated at 600 °C in ammonia atmosphere. Further, $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}:\text{N}-600$ NWs exhibited excellent photoelectrochemical stability under illumination compared to pure ZnO NWs. These promising results suggest the potential of $(\text{Zn}_{0.95}\text{Co}_{0.05})\text{O}:\text{N}-600$ NWs as a viable photoanode in PEC water splitting cell. Additionally, theoretical first principles

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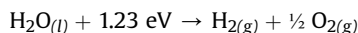
study conducted explains the beneficial effects of Co and N co-doping on both, the electronic structure and the band gap of ZnO.

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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-carbonaceous resources such as water is very much desired, as it does not produce any undesired 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 also uses high temperature ($\geq 1000 \text{ }^{\circ}\text{C}$) 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 adaptation of thermolysis of water on an 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 electricity driven water splitting (i.e., water electrolysis) seems 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 driving the water splitting reaction (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 pioneering 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 (1.23 V vs NHE) and reduction potential of water (0 V vs NHE) lie within the band gap of the material [9]. TiO₂ has been largely and extensively explored 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 of 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 ease of 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 (~155 cm² V⁻¹ s⁻¹ for ZnO vs ~10⁻¹ cm² V⁻¹ s⁻¹ for TiO₂) [35–40]. However, the wide band gap (~3.2 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 dopants [41–45]. Such a doping strategy is expected to improve the photoelectrochemical performance due to improved light absorption occurring as a result of a decrease in the band gap and increase in number of carriers available for reaction. However, the selection of suitable dopants and their concentration is important for tailoring the band structure of ZnO. Though high concentrations of dopants 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 further 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 despite these advances for ZnO based semiconductor materials 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 the 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 based photoanodes.

Cobalt is considered herein as a promising dopant for ZnO, on the grounds of the observed red-shift in the light absorption to the

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