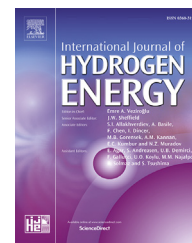




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# Electrochemically active and robust cobalt doped copper phosphosulfide electro-catalysts for hydrogen evolution reaction in electrolytic and photoelectrochemical water splitting

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## ABSTRACT

The area of non-noble metals based electro-catalysts with electrochemical activity and stability similar or superior to that of noble metal electro-catalyst for efficient hydrogen production from electrolytic and photoelectrochemical (PEC) water splitting is a subject of intense research. In the current study, exploiting theoretical first principles study involving determination of hydrogen binding energy to the surface of the electro-catalyst, we have identified the  $(\text{Cu}_{0.83}\text{Co}_{0.17})_3\text{P}:x$  at. % S system displaying excellent electrochemical activity for hydrogen evolution reaction (HER). Accordingly, we have experimentally synthesized  $(\text{Cu}_{0.83}\text{Co}_{0.17})_3\text{P}:x$  at. % S ( $x = 10, 20, 30$ ) demonstrating excellent electrochemical activity with an onset overpotential for HER similar to Pt/C in acidic, neutral as well as basic media. The highest electrochemical activity is exhibited by  $(\text{Cu}_{0.83}\text{Co}_{0.17})_3\text{P}:30$  at. % S nanoparticles (NPs) displaying overpotential to reach  $100 \text{ mA cm}^{-2}$  in acidic, neutral and basic media similar to Pt/C. The  $(\text{Cu}_{0.83}\text{Co}_{0.17})_3\text{P}:30$  at. % S NPs also display excellent electrochemical stability in acidic media for long term electrolytic and PEC water splitting process [using our previously reported  $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ : N-600 nanotubes (NTs) as the photoanode]. The applied bias photon-to-current efficiency obtained using  $(\text{Cu}_{0.83}\text{Co}_{0.17})_3\text{P}:30$  at. % S NPs as the cathode electro-catalyst for HER in an H-type PEC water splitting cell (~4%) is similar to that obtained using Pt/C (~4.1%) attesting to the promise of this exciting non-noble metal containing system.

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## Introduction

Achieving sustainable, economic and clean energy supply by replacing hitherto technologies for energy production based on combustion of fossil fuels is one of the major energy related technological hurdles facing the globe today [1–6]. Incessant large dependence and consequent, vast consumption of fossil fuels has contributed to excessive emissions of greenhouse gases which has led to global climatic changes over the years placing significant stress on the environment [1–5]. Hence, at the risk of significantly compromising the environment, it is imperative to identify efficient, clean (low carbon footprint) and environmentally friendly energy sources that can be manufactured and produced in an economical fashion. This will enable the society to transition from an energy economy driven largely by fossil fuel based energy sources to non-carbonaceous fuels based economy with the aim of meeting the colossal global energy demand with minimum emission of greenhouse gases and thus, ensuring a sustainable society driven by environmental recyclable resources of solar, wind, and water [1,4,7–12]. Along these lines, hydrogen has been identified as the primary potential energy source due to its low carbon footprint, high energy density (120 MJ/kg for H<sub>2</sub> higher than 44.4 MJ/kg for Gasoline) and the ability to offer clean, reliable and affordable energy supply for meeting the tremendous global energy demand [13]. In addition, hydrogen is an important chemical with a global production rate of 50 billion kg per year that is mainly used in petroleum refining and production of ammonia based fertilizers as well as other important industrial chemicals [14].

Current approaches for H<sub>2</sub> production mainly involve steam reforming of natural gas, coal gasification and the partial oxidation of hydrocarbons [15,16]. The drawbacks of these processes are high operating temperature and emission of CO<sub>2</sub>, the undesired greenhouse gas pollutant [15,16]. With the increase in global demand of H<sub>2</sub> on the grounds of its important applications mentioned above, processing of vast amount of fossil fuels is not viable. Hence, it is of utmost importance to produce hydrogen from non-carbonaceous and environmentally friendly tools with minimum emission of greenhouse gases.

Electricity driven water splitting (water electrolysis coupled to renewable energy source such as solar, wind, etc.) and photoelectrochemical (PEC) water splitting (where electricity is generated from suitable semiconductor material used as the photoanode and then used in tandem to drive the HER to produce H<sub>2</sub> at the cathode) are promising approaches, as they involve production of hydrogen from non-carbonaceous sources with no emission of greenhouse gases whatsoever and no toxic byproducts [17,18]. In these processes, electricity is used for driving the water splitting reaction ( $\Delta G^\circ = 237.13 \text{ kJ mol}^{-1}$  or 1.23 eV) [19]. However, one of the factors limiting the commercial development of electrolytic water splitting process is the high capital cost, mainly due to the use of expensive precious noble metal electro-catalysts (e.g. Pt, IrO<sub>2</sub>) that albeit exhibit excellent electrochemical activity with minimum overpotential and long term electrochemical stability. The development of PEC water splitting systems is however, constrained by insufficient solar-to-

hydrogen (STH) efficiency and limited long term stability. Moreover, the use of noble metal electro-catalysts (Pt, Pd) could be a concern for future applications in PEC systems.

The development of novel non-noble metals based electro-catalyst exhibiting similar/superior electrochemical activity with minimum overpotential and stability than state of the art electro-catalyst (Pt/C) for hydrogen evolution reaction (HER), which constitutes half of the water splitting reaction, will be a significant breakthrough in reduction of capital cost of water splitting cells. In addition to proton exchange membrane (PEM) based water electrolysis and PEC water splitting involving operation in acidic media (pH=0), HER is also very important in the microbial electrolysis cell (MEC) which involves production of hydrogen from wastewater (neutral media, pH=7) through microbes assisted degradation of organic waste and electrolytic water splitting for generation of hydrogen in basic media (pH=14) [20]. An ideal non-noble metals based HER electro-catalyst should exhibit superior electrochemical active surface area, high electronic conductivity, superior charge transfer kinetics, high current density at low overpotential, excellent electrochemical activity for HER and superior long term electrochemical stability for continuous H<sub>2</sub> production over long period of operation in acidic, neutral as well as basic media.

In the pursuit of identification and development of cheap, highly electrochemically active and stable electro-catalysts for HER, there have been many pioneering studies reported on non-noble metals based nitride and sulfide based electro-catalysts exhibiting promising performance for HER such as MoS<sub>2</sub> [21,22], CoSe<sub>2</sub> [23], Co<sub>0.6</sub>Mo<sub>1.4</sub>N<sub>2</sub> [24], MoSe<sub>2</sub> [25], NiMoN<sub>x</sub> [26], WS<sub>2</sub> [27], etc. Earth-abundant transition metal phosphides (TMPs) are also important materials exhibiting good electronic conductivity and are widely utilized as catalysts in hydrodesulfurization (HDS), hydrodenitrogenation as well as anode materials for Li ion batteries [28–32]. Both HDS and HER rely on reversible binding of hydrogen on the catalyst surface. In HDS, hydrogen dissociates on the catalyst surface and reacts with sulfur forming H<sub>2</sub>S which creates a reactive sulfur vacancy site [14], while in HER, the protons bind to the electro-catalyst surface promoting HER and accordingly generating H<sub>2</sub> gas [28]. Thus, TMPs are also considered as active electro-catalysts for HER. On the basis of these developments, there has correspondingly been significant research efforts directed to the study of TMPs as electro-catalysts for HER such as Ni<sub>2</sub>P [33,34], CoP [20,28,35,36], MoP [37], FeP [32,38], WP [39], WP<sub>2</sub> [40], etc., wherein, these electro-catalysts have shown noticeable electrochemical activity for HER.

With the principle aim of this study targeted at the design and development of cheap non-noble metals based electro-catalysts displaying similar/superior electrochemical activity for HER and stability than that of Pt/C, in this report we describe copper phosphide (Cu<sub>3</sub>P) based electro-catalyst system that has been studied as a potential electro-catalyst for HER, on the grounds of promising HER performance displayed by self-supported Cu<sub>3</sub>P nanowire arrays [41]. In the present study, therefore, theoretical first-principles electronic structure calculations involving determination of the hydrogen binding energy ( $\Delta G_{\text{H}^*}$ ) to the surface of specific electro-catalysts, has been carried out to identify and develop

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