

ADVANCEMENTS IN TRANSITION METAL-DOPED ELECTRO-CATALYSTS: CO AND MN DOPED ZNO NANOPARTICLES FOR COST-EFFECTIVE HYDROGEN PRODUCTION

Seemab Altaf^{*1}, Dr. Muhammad Ali Mohsin²

^{*1}M. Phil Chemistry, University of Lahore, Pakistan

²PhD Chemistry, University of Lahore, Pakistan

^{*1}greenpak247@gmail.com, ²muhammad.mohsin@chem.uol.edu.pk

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Corresponding Author: *

Seemab Altaf

Abstract

One of the most favorable method for storage of sustainable energy and the society hydrogen realization in the near future is the production of hydrogen by the process of electrochemical water parting. However, the strategic for the large-scale utilization of this method is to produce cheap and much effective electro-catalyst in order to reduce the use of expensive noble metals. Therefore, a variety of bi-functional electro-catalysts based on transition metals for both cathode and anode have previously been established for overall process of water splitting. Herein, we report the use of Co and Mn doped ZnO nanoparticles prepared by hydrothermal method. It was investigated that the doped zinc oxide nanoparticles are in hexagonal shaped with size in the range of few nm. Comparative XRD, SEM and EDX studies revealed that Co²⁺ and Mn²⁺ are uniformly doped into the crystal structure of ZnO. Later on, it was observed that these nanoparticles exhibit excellent efficiency towards water splitting process for the production of hydrogen. It was clear from the results that these electro catalysts were much efficient in order to overcome the energy of activation for the overall process and to reduce the value of over potential.

I. INTRODUCTION

Renewable and sustainable sources of energy have never been more needed in the world as the world energy demands keep drawing higher and fossil fuel reserves allow a rapid depletion. Fossil fuels that are traditional not only lead to the depletion of non-renewable resources but also worsen such problems as sludge pollution, global warming, and climate change (Zhang et al., 2020). In order to deal with these issues, it has seen a major transition to natural energy sources including solar, wind energy and hydropower. Hydrogen is one of these and a promising energy carrier because of its high energy density, clean combustion, and its ability to use hydrogen in multiple applications, including fuel cells, which

are central to eliminating carbon footprint of the transportation and power sectors (Li et al., 2020). Hydrogen is thought to be among the most efficient energy carriers, and its energy density per kilogram (120 MJ/kg) compares to traditional fuels such as gasoline (44 MJ/kg) by far (Wang et al., 2019). Moreover, hydrogen fuel cells do not emit any gases except water and heat; hence, they are also environmentally friendly as compared to conventional technologies that operate on combustion (Peng et al., 2020). However, there are big obstacles to the widespread implementation of hydrogen as a source of energy, mostly associated with its manufacturing, storage, and infrastructure. Hydrogen cannot be found

naturally on Earth, and it has to be produced via different methods, such as electrolysis, steam methane reforming, and biomass gasification (Zhang et al., 2020). One of these approaches, electrochemical water splitting has been one of most prospective methods of hydrogen production because it provides a direct non-pollutant and long lasting method of producing hydrogen out of water through electricity.

Hydrogen Production through Electrochemical Water Splitting.

Electrochemical water splitting involves the use of an electric current to split water (H_2O) into hydrogen (H_2) and oxygen (O_2) gases. This is done in an electrolyzer, made up by two electrodes namely an anode and cathode, separated by an electrolyte. Electric current is used to split the water molecules, producing hydrogen at the cathode (hydrogen evolution reaction, HER), and oxygen at the anode (oxygen evolution reaction, OER). This process is very sensitive in terms of the performance of electrodes and the electrolyte employed. Although theoretically, the lowest voltage needed to perform electrolysis is 1.23 V, a higher voltage is needed in reality to compensate for the loss of energy due to numerous components, such as the activation energy of electrodes, resistance, and overpotentials (Wang et al., 2019). This translates to a large energy consumption loss when electrolyzing the water and this is a huge constraint to the extensive use of water splitting as a huge hydrogen production process.

The selection of electro-catalysts is one of the most crucial factors that affect the efficiency of the electrochemical process of splitting water. Electrocatalysts are materials that enhance the rate of the hydrogen and oxygen evolution reactions (HER and OER). During decades, the most efficient electrocatalysts to carry out these reactions have been platinum (Pt) and iridium (Ir), as they are highly conductive and reduce overpotentials (Li et al., 2020). Nonetheless, these noble metals are very expensive, scarce and of limited numbers hence rendering them impractical in large-scale production of hydrogen.

Non-Noble Metal Electro-Catalysts.

Researchers in recent years have been looking into the development of non-noble metal-based electrocatalysts, which are not only cost-effective, but also greatly able to catalyze the water splitting process. Cobalt (Co), manganese (Mn), nickel (Ni), and iron (Fe) cover the category of transition metals that has received considerable attention due to their abundance on earth, cheaper cost, and good catalytic capacity of both HER and OER (Zhang et al., 2020). However, these materials are usually associated with low stability, low conductivity and high overpotentials in contrast to noble metals. Researchers have been investigating different options to overcome these shortcomings and have considered doping, alloying, and development of hybrid systems to improve the catalytic activity of non-noble metal catalysts. One method and practice that are especially successful in enhancing the performance of electrocatalysts is doping. Doping may alter the electronic structure, add active sites, and improve conductivity of the catalyst by incorporating foreign atoms into the metal lattice (Wang et al., 2019). Zinc oxide (ZnO) is a promising semiconductor material, which has demonstrated potential in the electrochemical field because it has very good electronic properties, stability, and availability. However, catalytic activity of pure ZnO is limited when it comes to catalyzing water splitting reactions because it possesses a large bandgap of the material and has poor charge carrier mobility (Peng et al., 2020). ZnO may also be doped with a transition metal that can improve its electro-catalytic properties, including cobalt (Co) and manganese (Mn). The doping of ZnO nanoparticles with Co and Mn has demonstrated high improvements in the catalytic activity, decreased overpotentials, and better stability relative to undoped ZnO (Li et al., 2020).

Co and Mn Doped ZnO Nanoparticles as Electro-Catalysts.

The study seeks to study the usage of Co and Mn-doped ZnO nanoparticles as electro-catalysts in the water splitting process. Doping of ZnO with Co and Mn improves the electronic structure of the sample, the number of active sites, and the transfer of charge during the electrolysis process. The Co and Mn-doped ZnO nanoparticles revealed have superior catalytic efficiency in both the HER and

OER with lower overpotentials and higher efficiency than pure ZnO (Zhang et al., 2020). Co and Mn-doped ZnO nanoparticles are mainly synthesized by a hydrothermal process, and the dopants are distributed evenly throughout the ZnO lattice. The successful growth of ZnO as doped and to investigate the size, shape and composition of the nanoparticles is confirmed by characterization technology i.e. the X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The Co and Mn dopants do not only increase the electronic properties of ZnO, but they also contributed to stabilizing the structure and enhancing it in durability and performance during a long time of use (Peng et al., 2020).

Hydrogen is gaining more recognition as a crucial remedy to the world energy crisis because it has clean and efficient characteristics. Splitting water electrochemically is one of the long-term solutions to the problem of hydrogen production, yet the inefficiency and high cost of existing electrocatalysts are significant challenges. The study aims at synthesizing Co and Mn-doped ZnO nanoparticles as electrocatalysts with non-noble and economical properties in water splitting. The process of doping has improved the catalytic properties of ZnO, decreased overpotentials, and improved the efficiency of hydrogen production making it an attractive candidate in large-scale hydrogen production. This study enhances the production of less expensive and efficient hydrogen production techniques that will help facilitate the shift to a sustainable energy future due to the further development of non-noble metals catalysts.

II. Literature Review

A shift towards renewable and sustainable energy sources is very much needed because fossil fuels are very slow to renew, and the effects of their use are increasingly detrimental to the environment (Zhang et al., 2020). Hydrogen is considered to be one of the most promising renewable energy carriers since the energy density is quite high, and it is more environmentally friendly than other energy carriers (Li et al., 2020). When applied as fuel cells, Hydrogen generates nothing more than water and heat as by-products, thus it is a friendly

substitute to fossil fuels that doesn't harm the environment (Wang et al., 2019). In addition, hydrogen is the most plentiful in the universe and can be produced using water, which occupies nearly 71 out of the 100 percent of the surface of the Earth, which means it is an almost inexhaustible source (Peng et al., 2020). Some of the ways in which hydrogen can be manufactured are by reforming methane on steam, gasifying biomass and electrochemical splitting of water. One of the most sustainable hydrogen production methods is regarded as electrochemical water splitting, i.e., the utilization of electricity to break down water into hydrogen and oxygen (Zhang et al., 2020). The approach, however, is beset with considerable difficulties in energy efficiency and cost, mostly because of the requirement of a high-performance electro-catalyst of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) (Peng et al., 2020).

Electrochemical processes Water Splitting Process.

One of the processes involving an electric current to separate water into oxygen and hydrogen gases is electrochemical water splitting. This reaction is achieved in an electrolyzer with the oxidation of water on the anode to produce oxygen and the reduction of water on the cathode to produce hydrogen (Wang et al., 2019).

Although theoretically the minimum voltage needed for electrolysis is 1.23 V, in reality, more power is needed to overcome numerous inefficiencies and activation energies involved in the reactions at the electrodes (Li et al., 2020). These inefficiencies are called overpotentials, and these characteristics of the HER and OER are major limiting factors to the efficiency of the electrochemical process of splitting water.

Water Splitting Electrocatalysts.

Electrocatalysts are important electrochemical process that significantly reduce the energy barriers of the HER and OER. The selection of electro-catalyst greatly determines the efficiency of water partitioning. Platinum (Pt) and iridium (Ir) have traditionally been the most successful electrocatalysts to use in these reactions since they have excellent conductivity and can reduce overpotentials (Li et al., 2020). However, these

noble metals are very expensive, scarce, and limited; therefore, they cannot be used to produce a lot of hydrogen (Wang et al., 2019). Consequently, the interest in working out non-noble metal-based electrocatalysts as a means of separating water has been increasing. Nickel (Ni), cobalt (Co), and iron (Fe), considered to be the candidates due to their abundance, low cost, and fairly good catalytic activity (Peng et al., 2020). Although superior in some aspects, these non-noble metals tend to be less catalytic, unstable, and have a greater overpotential than noble metals (Li et al., 2020). Thus, optimization of the performance of these materials in terms of different procedures including doping, alloying and hybridization has become an important area of research nationally in the recent past.

Transition Metal-Based Electrocatalysts

Due to their desirable electrochemical characteristics, transition metals have been widely investigated in its capacity to be applied in water splitting reactions. The nickel and cobalt are especially good candidates to replace the HER as they have high catalytic activity and are inexpensive as well. Nonetheless, such metals tend to have low conductivity and stability throughout their extended application (Wang et al., 2019). To deal with these shortcomings, scientists have aimed at doping these metals with other elements to give them better electrochemical performance. One of the most popular methods of increasing the properties of the electrocatalysts is doping. Doping can modify the electronic structure, enhance the number of active sites, and enhance the overall conductivity of the catalyst by introducing foreign atoms into the crystal lattice of transition metals (Zhang et al., 2020). One example is co doping cobalt (Co) with other transition metals such as manganese (Mn) or iron (Fe) which is demonstrated to enhance the catalytic activity and stability of the catalyst of the HER as well as the OER (Li et al., 2020).

ZnO as Semiconductor Electrocatalyst.

Zinc oxide (ZnO) is a semiconductor material that has demonstrated the ability to be utilized in electrochemical processes, such as splitting of water. ZnO is highly favored due to its good stability, non-toxicity, and profuseness; therefore,

it is an appealing material in the development of electro-catalysts (Peng et al., 2020). However, ZnO in its pure form is not an effective catalyst to split water because it has a large bandgap and low charge mobility, resulting in inefficient separation of charge during electrolysis. Researchers have been looking into doping ZnO with some of the transition metals such as cobalt (Co) and manganese (Mn) in order to improve the electro-catalytic properties of ZnO. It was demonstrated that the doping of ZnO with Co and Mn enhances its electronic properties, lowers overpotentials, and boosts its catalytic activities of the HER and OER (Wang et al., 2019). ZnO nanoparticles decorated with Co and Mn will have enhanced charge transfer and surface area, all other important parameters in enhancing the efficiency of electrochemical water splitting (Zhang et al., 2020).

Preparation of Co and Mn-Doped ZnO Nanoparticles.

Synthesis of Co and Mn-doped ZnO nanoparticles is usually done using hydrothermal, sol-gel, and co-precipitation techniques. The most common of them is the hydrothermal technique, which successfully generates uniform and well-spread nanoparticles, having a controlled size and morphology (Peng et al., 2020). The doping is done; Co and Mn are introduced into the crystal structure of ZnO that changes the electronic properties of this material and makes it better in catalysis. They use characterization methods like X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) to determine the successful doping of ZnO with Co and Mn and assess the size, shape, and composition of the nanoparticles (Li et al., 2020). The XRD results are usually characteristic peaks associated with hexagonal form of ZnO whose diffraction peaks shifted upon introducing Co and Mn ions into the ZnO structure (Zhang et al., 2020). SEM images will be used to report the morphology of the nanoparticles, while the uniform distribution and elemental composition of the dopants will be verified using EDX.

Literature Gap

Although the study has yielded positive outcomes with Co and Mn-doped ZnO, in the literature, there are still several gaps in the scalability, stability over time, and the mechanism of these catalysts. Although the enhanced catalytic role of Co and Mn-doped ZnO is proven by numerous experiments, the majority of them are conducted in small-scale laboratory tests, and little research involved how the efficacy of these catalysts can be increased to fit the industrial setting (Peng et al., 2020). Furthermore, it is not clear whether Co and Mn-doped ZnO nanoparticles are stable under real-world working conditions as most catalysts are not robust to the harsh electrochemical conditions (Zhang et al., 2020). The other important gap in the literature is in-depth mechanistic knowledge to explain how doping Co and Mn into ZnO is used to improve its catalytic activity. Though some investigations have demonstrated the enhanced performance in terms of reduced overpotentials and increased rates of hydrogen production, the specific mechanism through which Co and Mn affect the electronic structure of ZnO and promote catalytic performance is not yet clear (Wang et al., 2019). Additional research is required on the electronic characteristics, charge transfer processes and the atomic-molecular part played by the dopants in the catalytic reactions.

Moreover, although doping Co and Mn have been demonstrated to enhance the electrochemical characteristics of ZnO the synthesis processes and conditions should be further optimized to achieve reproducibility and homogenization of the nanoparticles. The performance of the catalysts can notably be affected by variations in doping level, the temperature of synthesis, and the material used, and further studies can be required to determine the best synthesis methods to use during large-scale manufacturing (Li et al., 2020). Electrochemical conversion of water to hydrogen also has tremendous potential of being a green and affordable source of energy. The cost and performance of electrocatalysts, however, still limits the efficiency of this process. ZnO nanoparticles with transition metal impurities, especially Co and Mn-impure ZnO, have recently become a promising non-noble metal catalyst in splitting of water as they are inexpensive,

abundant, and more catalytic. Although a lot has been achieved in the electro-catalytic characteristics of these materials, there are still gaps in the system, especially scaling, long-term stability and understanding of the mechanism characterizing their catalytic activity. It is important that such gaps will need consideration to allow the large-scale realization of this hydrogen production through electrochemical splitting of water.

III. Methodology

The research design is based on the synthesis, characterization process, and electrochemical analysis of Co and Mn-doped ZnO nanoparticles as electrocatalysts of the electrochemical splitting of water process. The method consists of several steps and the synthesis of doped ZnO nanoparticles, overall characterization, via various methods, and the assessment of their catalytic activity in splitting water. The methodology permits the synthesis of the nanoparticles to be reproducible and scaled, as well as ensuring the electrochemical properties are measured correctly in order to assess the effectiveness of such materials in hydrogen production.

Co and Mn-Doped ZnO Nanoparticles synthesis.

Co and Mn-doped ZnO nanoparticles will be synthesized by hydrothermal. This method is well known to yield homogenous nanoparticles of controlled size and shape that are critical to high-performance electrocatalysts (Li et al., 2020). Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) will be used as the source of ZnO in the research and cobalt chloride (CoCl_2) and manganese chloride (MnCl_2) will play the role of dopants in Co and Mn respectively.

The procedure entails the preparation of an aqueous solution in which the stoichiometric quantities of zinc acetate, cobalt chloride and manganese chloride are combined. This solution will be followed by the addition of sodium hydroxide (NaOH), to maintain the desired pH and then transferred into a Teflon lined autoclave in which the solution will undergo hydrothermal treatment at 180°C after 12 hours. The product will be cooled to room temperature after the reaction, washed using distilled water and ethanol before being dried at 60°C at 24 hrs. They will be

used to test different doping concentrations of Co and Mn (e.g., 1,3,5 percent of Co and Mn compared to Zn) to make sure that the concentration of doping elements is the same. The resulting product will be characterized to establish the addition of Co and Mn into ZnO lattice, as well as the size, morphology and surface area of the nanoparticles.

Characterization of Co and Mn-Doped ZnO Nanoparticles

To confirm structural, morphological, and compositional properties of the Co and Mn-doped ZnO nanoparticles, several techniques will be utilized to characterize it.

X-ray Diffraction (XRD): The crystal structure and purity of the crystals of the synthesized nanoparticles in terms of purity will be determined using XRD. The patterns of diffraction will be used to establish the structure of ZnO as hexagonal wurtzite, and to establish successful incorporation of Co and Mn ions in the ZnO structure. To measure the degree of doping, changes in the diffraction peaks will be followed (Wang et al., 2019).

Scanning Electron Microscopy (SEM): SEM will be used to examine the morphology of the nanoparticles. The procedure will give a high-resolution image of the surface morphology, particle size, and a homogeneity of the nanoparticles (Li et al., 2020).

Energy Dispersive X-ray Spectroscopy (EDX): To ascertain the elemental composition of the nanoparticles, EDX will be employed. Co and Mn presence and distribution in the ZnO nanoparticles will be checked using this technique (Peng et al., 2020).

Transmission Electron Microscopy (TEM): The fine details of the nanoparticle structure will be observed by TEM, which will provide information on the size of the particles, crystallinity, and the distribution of the dopants at the nanoscale (Zhang et al., 2020).

Brunauer-Emmett-Teller (BET) Surface Area Analysis: BET analysis will be done to measure the surface area and porosity of the nanoparticles. Increasing the number of active sites to the electrochemical reactions is important, which is achieved by having high surface area (Wang et al.,

2019).

X-ray Photoelectron Spectroscopy (XPS): XPS will be used to investigate the surface composition and chemical states of the Co and Mn dopants in the ZnO nanoparticles. This method will give crucial information on the oxidation configuration of Co and Mn, which are important to comprehend their catalytic activity (Peng et al., 2020).

Electrochemical Evaluation

Electrochemical characteristics of Co and Mn-doped ZnO nanoparticles will be assessed under three-electrode system works based on the following techniques; cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry. A three electrode setup is going to be used, comprising of:

Working Electrode: Co and Mn-doped ZnO nanoparticles will be drop-casted on a glassy carbon electrode (GCE). The catalyst ink will be made by dispersion of the nanoparticles in solution Ethanol and Nafion. The dispersed solution will be sonicated to achieve a homogeneous distribution of the nanoparticles and then drop-cast on the GCE.

Counter Electrode: This will be a platinum wire of counter electrode.

Reference Electrode: A saturated calomel electrode (SCE) will be used as the reference electrode.

The electrochemical analysis will be conducted using the 0.5 M KOH aqueous solution to recreate the alkaline electrochemical conditions that are used in the common water splitting process (Zhang et al., 2020).

Cyclic Voltammetry (CV): CV will be performed to evaluate the electrochemical stability and the electrochemical active surface area (ECSA) of the Co and Mn-doped ZnO catalysts. The onset potentials of the HER and OER, as well as the current density will be measured on CV curves, which are the crucial parameters that reflect the performance of the catalyst (Peng et al., 2020).

Linear Sweep Voltammetry (LSV): LSV will be used to determine the catalytic activity of the Co and Mn-doped ZnO catalysts for both the HER and OER. The overpotentials of the two reactions will be recorded and compared with that of a commercial platinum electrode that will be used

in the HER reaction and an iridium oxide electrode that will be used in the OER reaction (Li et al., 2020).

Chronoamperometry: To determine the stability of Co and Mn-doped ZnO catalysts in the long run, chronoamperometry will be used. The long-term performance of the catalysts will be observed at long durations to assess the long-term serviceability and performance of catalysts under the running electrolysis phase (Zhang et al., 2020).

Performance Comparison

The catalytic performance of the Co and Mn-doped ZnO nanoparticles will be compared to that of pure ZnO and other benchmark catalysts, such as platinum and iridium oxide. The main parameters, such as overpotentials, catalytic efficiency, stability, will be analyzed and compared to decide whether the Co and Mn-doped ZnO nanoparticles will be suitable in the case of large-scale hydrogen production (Wang et al., 2019).

IV. Results

This chapter consists of information related to instruments and chemicals used alongside the method of preparation, techniques for characterization and applications conducted during this study.

Chemicals

Analytical grade reagents were used during the experimental work without further purification. Zinc oxide was received from Riedel de Haen, China, manganese (II) Sulphate 1-hydrate and Cobalt (II) chloride were provided by Sigma Aldrich, Germany. Hydrochloric acid (37 % purity) was also obtained from Riedel de Haen, China, and distilled water.

Preparation of solutions

The solution of zinc oxide, copper chloride and manganese sulphate. was prepared. Each of these chemicals was first dissolved in distilled water and shaken until a clear 1M solution of each salt was obtained.

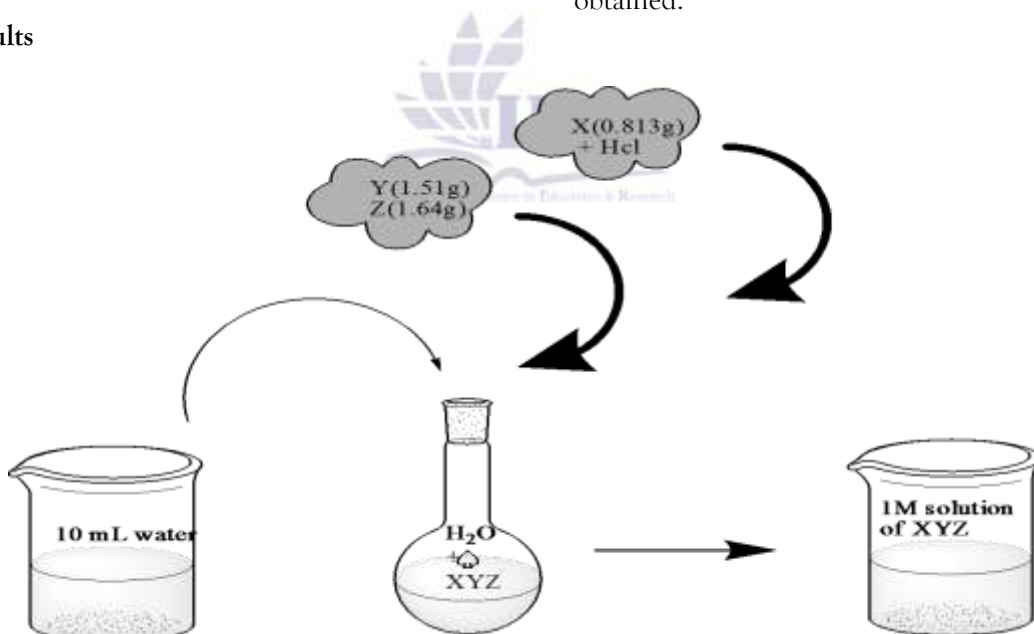


Figure 1.1 General scheme for preparation of 1M solution of XYZ where, X=ZnO, Y=MnSO₄ and Z=CoCl₃

Preparation of ZnO solution

1M ZnO solution was prepared by dissolving 0.813g of ZnO in 10ml of distilled water. As ZnO is insoluble in water therefore few drops of conc. HCl was also added. The mixture was then shaken until a clear solution of ZnO was obtained.

Preparation of MnSO₄ solution

1M MnSO₄ solution was prepared by dissolving 1.51g of MnSO₄ in 10ml of distilled water. The mixture was then shaken until a clear solution of

MnSO₄ was obtained

1.64g of CoCl₃ in 10ml of distilled water. The mixture was then shaken until a clear solution of CoCl₃ was obtained.

Preparation of CoCl₃ solution

1M CoCl₃ solution was prepared by dissolving



Figure 1.2 Preparation of 1M solutions of ZnO, CoCl₃ and MnSO₄

Cleaning of autoclave

First of all autoclave was cleaned thoroughly. The cleaning process was performed by dipping all the parts of autoclave in 500 ml of beaker which was filled with chromic acid solution. After washing with chromic acid solution it was then washed with ethanol/methanol solution. It was then washed with distilled water. Then dried it in open air. The autoclave was then ready to use.

Preparation of sample solution

By using already prepared 1M solutions of ZnO, MnSO₄ and CoCl₃ in 10 ml of distilled water, the samples were prepared in different ratios. A total of 13 samples in different ratios were prepared by using hydrothermal method. Out of these 13 samples seven samples consists of Mix

ratios, three samples was reference samples and remaining three samples was test samples.

Preparation of sample CMZ x (x = 1,2,3.....13) (C = CoCl₃, M = MnSO₄, Z = ZnO)

All samples were prepared comprises of various ratios of Co: Mn : Zn respectively by hydrothermal method which was performed in an autoclave. All the three solutions were mixed in different ratios in a beaker. Then poured this solution in teflon chamber carefully. The teflon chamber must be filled $\frac{3}{4}$ of its total volume and then it was properly closed. Then teflon chamber was placed in stainless steel reactor. The inner walls of reactor lid as well as outer walls of reactor were lubricated well with grease or any other lubricant so that it was opened easily. reactor lid was closely tightened; screw rod was used to tighten up until locking.



(a) (b)

Figure1.3 (a) Clear NPs after autoclave heating. (b) NPs collected at the bottom of centrifuge tube after centrifugation

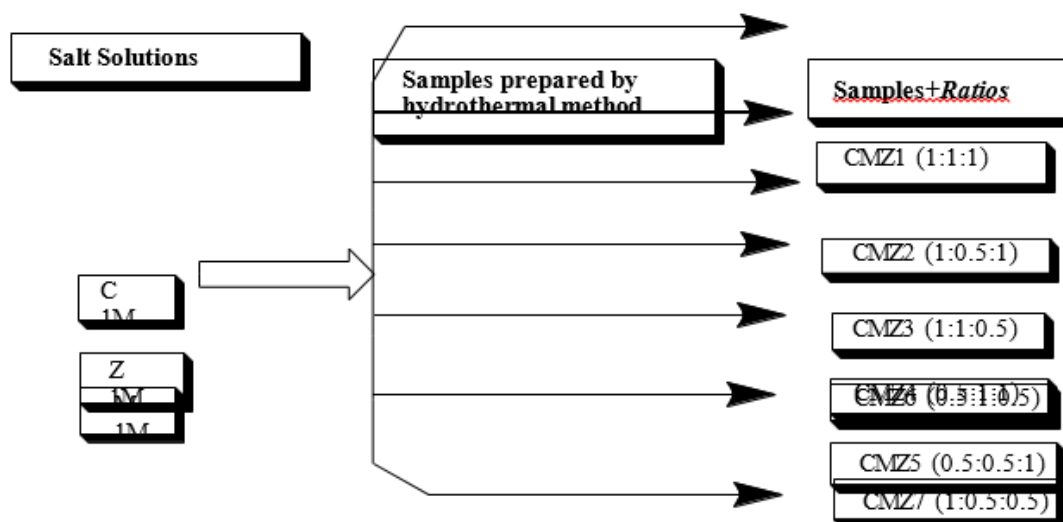


Figure.1.4 Schematic diagram for preparation of seven mix ratio samples where, C = CoCl_3 , M = MnSO_4 and Z = ZnO

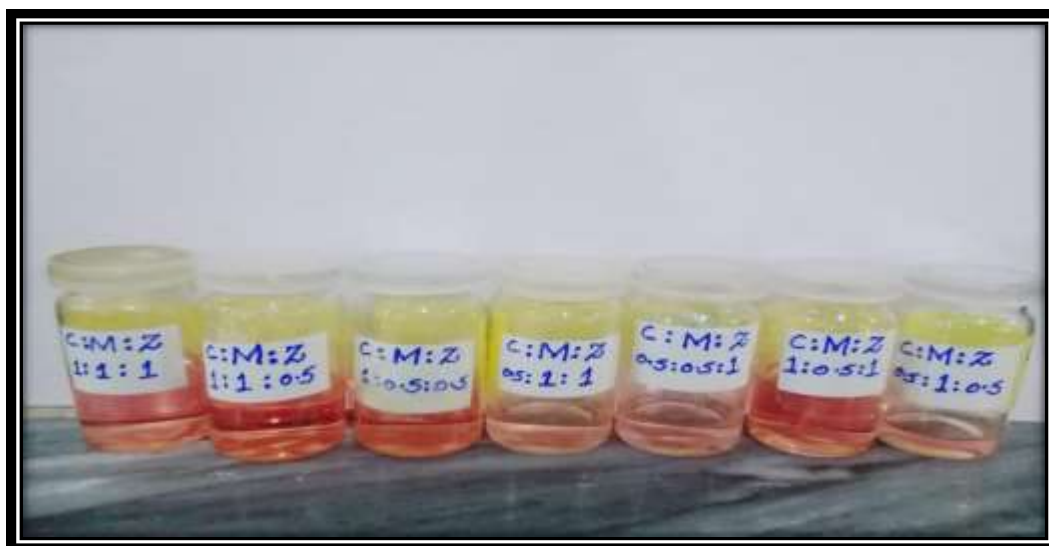


Figure.1.5 Preparation of seven mix ratio samples where C = CoCl_3 , M = MnSO_4 and Z = ZnO

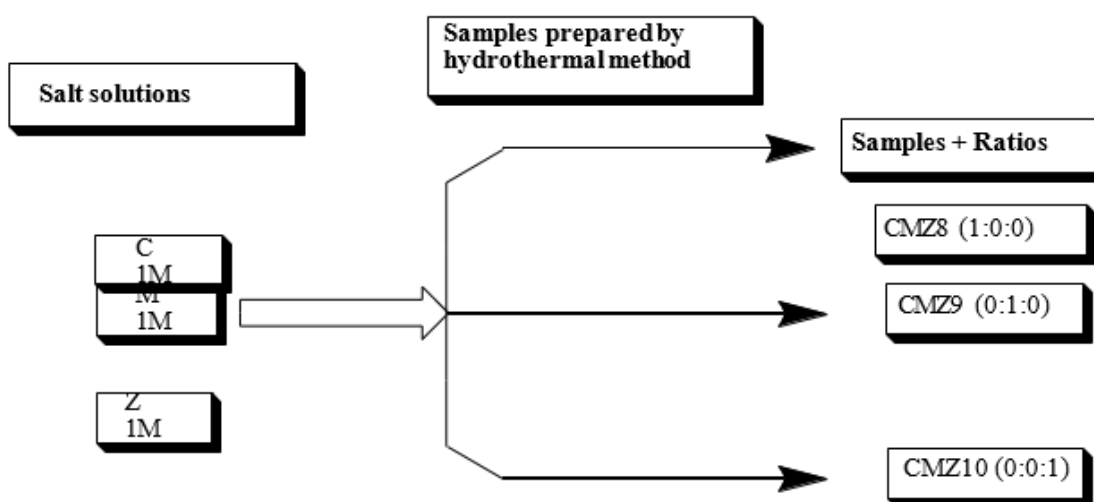


Figure.1.6 Schematic diagram for preparation of three reference samples where, C = CoCl_3 , M = MnSO_4 and Z = ZnO



Fig 1.7 Preparation of three reference samples where, Co = Cobalt chloride (CoCl_3), Mn = Manganese sulphate (MnSO_4), and Zn = Zinc oxide (ZnO)

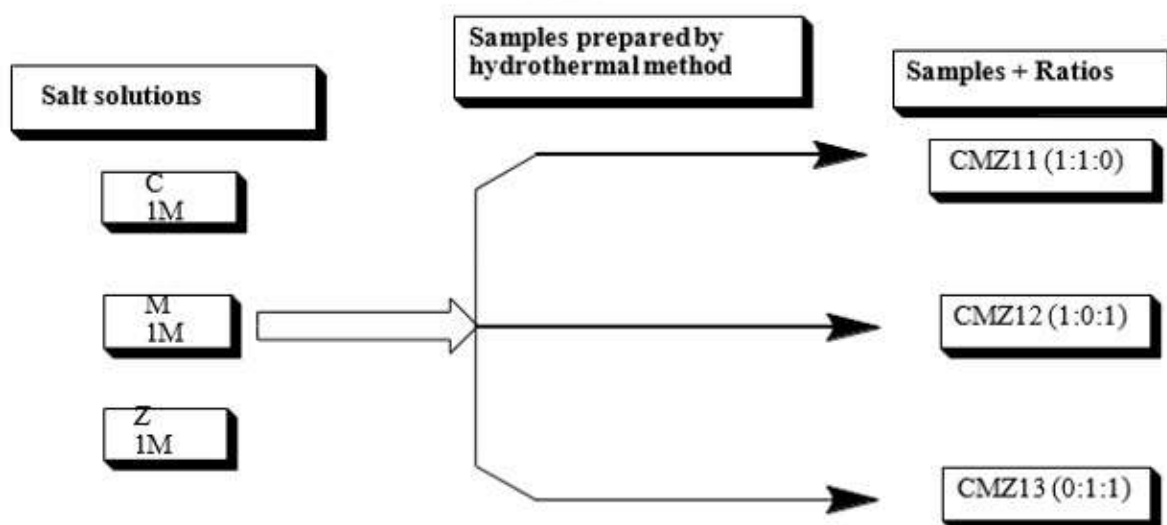


Figure.1.8 Schematic diagram for preparation of three test samples where, C = CoCl_3 , M = MnSO_4 and Z = ZnO



Fig 1.9.Preparation of three test samples where, Co = Cobalt chloride (CoCl_3), Mn = Manganese sulphate (MnSO_4), and Zn = Zinc oxide (ZnO)

V. Discussion

The analytical research in this study aims at the synthesis, characterization and electrochemical assessment of cobalt (Co) and manganese (Mn) doped zinc oxide (ZnO) nanoparticles as electrocatalysts in water splitting. The experiment has shown that doping of ZnO with some of the transition metals like Co and Mn can greatly enhance the electrochemical performance of the ZnO crystal to boost its catalytic ability in relation to hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The findings of the different techniques used in characterization such as the X-ray diffraction (XRD), the scanning electron microscopy (SEM) and the energy-dispersive X-ray spectrophotometry (EDX) proved to have successfully doped both Co and Mn onto the ZnO lattice, resulting in increased catalytic performance of the water splitting mechanism.

In spite of the encouraging results, this work has a number of significant implications and research directions to investigate. These are the mechanisms of the increased catalytic activity, long term stability under working parameters, scalability, the optimization of synthesis process towards industrial use.

Mechanistic Understanding of Doping Effects

Among the major results of this study is the enhancement of the electrochemical properties on Co and Mn-doped ZnO nanoparticles. But how these transition metal dopants improve the catalytic activity is a still open question. The study proves that Co and Mn are doped into the lattice of ZnO but additional studies are required to understand the atomic interactions between the dopants and the ZnO matrix. In particular, the effects that Co and Mn have on the electronic structure, the charge transfer process, and active site formation must be investigated in further detail. Further study may incorporate the use of more sophisticated methods like X-ray photoelectron spectroscopy (XPS) to examine the oxidation states of the dopants and their reactions with ZnO. Also, atomic-scale simulations may aid in the interpretation of the changes in electrons due to doping and give an even better understanding of how dopants cause the improvements in catalytic performance observed. The knowledge of these mechanisms will be essential in the design of more efficient electrocatalysts and it will be of great advantage in understanding how to more effectively incorporate doping strategies.

Co and Mn-Doped ZnO Nanoparticles Stability and Durability.

The next significant point which needs to be examined is the stability and durability of Co and Mn-doped ZnO nanoparticles around the real-life electrochemical conditions. Although the experiment also showed a good catalytic efficiency in terms of producing hydrogen, it is still unclear what happens to the catalyst after prolonged periods of use, particularly, under the extreme conditions of electrochemical reactions (e.g., high voltage, different pH).

Future research ought to concentrate on how these catalysts will react with time, especially with regard to structural stability and catalytic activity. The long-term effectiveness and degradation of the catalysts during sustained electrolysis can be evaluated by techniques, e.g. cyclic voltammetry (CV) and chronoamperometry. Moreover, the stability of Co and Mn-doped ZnO nanoparticles to various electrolytes including alkaline and acidic solutions should also be investigated. This will be used to identify how long-lasting these catalysts are in the corrosive conditions of the electrochemical environment in large-scale applications.

Scalability and Industrial Use.

Although the hydrothermal synthesis process employed in the study produces good quality Co and Mn-doped ZnO nanoparticles, one of the main issues is scalability. Nanoparticle synthesis under constant doping concentration and size control, which leads to the reproducibility of results, is needed in larger scale production. Although the current synthesis process is as effective as it is in a laboratory setting, it might fail to work with the industrial-scale production because of the cost-related issues, time constraints, and energy consumption.

The research of the future ought to be concerned with optimizing the synthesis approaches to increase its scalability and cost-effectiveness. More realistic solutions could be found by investigating alternative, more energy efficient synthesis methods like sol-gel, or co-precipitation processes that can provide more economical approaches to large-scale production. Also, Co and Mn-doped ZnO catalysts should be evaluated in real life, e.g., in

large-scale electrolyzer, in an effort to determine their usefulness in hydrogen production at a commercial scale.

Doping Concentration and Synthesis Parameters.

Optimization of the doping of Co and Mn in ZnO is another important area that can be a focus of future research. The experiment found out that various ratios of doping (Co:Mn:Zn) resulted in differences in the overactivity of the catalysts of which some ratios perform better than others. Nevertheless, the best doping rate and production conditions have not been determined. The impact of the different levels of doping on ZnO electrochemical performance should be systematically investigated in future studies. This may single out the synthesis of various Co and Mn doping ratios and assessing their catalytic efficiency in HER and OER. Also, the parameters of the synthesis (temperature, pH, reaction time, etc.) should be optimized to reach optimal performance in regards to efficiency and stability. Determining the best synthesis conditions will play a significant role in the commercialization process of Co and Mn-doped ZnO as an electrocatalyst of large scale hydrogen production.

Environmental Impact and Sustainability.

Since the electrochemical splitting of water into hydrogen is deemed as potential technology of generating sustainable energy, it is vital to determine the effects of Co and Mn-doped ZnO nanoparticles on the environment. Utilizing non-noble metal electrocatalysts to produce hydrogen is a more sustainable and cost-efficient approach to the more conventional methods of producing hydrogen using the very expensive noble elements such as platinum and iridium. The environmental footprint of the materials used, however, including Co and Mn should be evaluated.

VI. Future Research Implication

The future study needs to pay attention to the life cycle analysis (LCA) of Co and Mn-doped ZnO catalysts to determine their sustainability in general. This will involve estimating the effects of raw materials extraction on the environment, synthesis process and the spent catalysts disposal.

In addition, the possibility of recycling such materials after their disposal should be also considered so that the sustainability of the production of hydrogen driven by the electrochemical splitting of water can be further supported.

VII. Conclusion

The study prepared cobalt and manganese doped ZnO nanoparticles by using hydrothermal method. The as-prepared materials were analyzed by using various characterization techniques i.e XRD, SEM, EDX and the results obtained was then compared with the results reported in literature. It was clear from the results that the dopant was uniformly substituted onto the hexagonal crystal structure of ZnO with no

impurities were detected. SEM and XRD analysis were demonstrated that these nanocrystals possess good structural quality and are in single phase. Furthermore, it was observed that these nanoparticles exhibit excellent efficiency towards water splitting process for the production of hydrogen. As ideally the electrochemical water splitting process needs a potential of 1.23V, however in practical situations a significantly greater voltage typically more than 1.8V is required to reduce the activation energy barrier of electrolytic process. It was clear from the results that these electrocatalysts were much efficient in order to overcome the energy of activation for the overall process and to reduce the value of overpotential.

REFERENCES

1. Li, X.; Duan, X.; Han, C.; Fan, X.; Li, Y.; Zhang, F.; Zhang, G.; Peng, W.; Wang, S., Chemical activation of nitrogen and sulfur co-doped graphene as defect-rich carbocatalyst for electrochemical water splitting. *Carbon* 2019, 148, 540-549.
2. Joo, J.; Kim, T.; Lee, J.; Choi, S.-I.; Lee, K., Morphology-Controlled Metal Sulfides and Phosphides for Electrochemical Water Splitting. *Advanced Materials* 2019, 31 (14), 1806682.
3. Wang, K.; Sun, K.; Yu, T.; Liu, X.; Wang, G.; Jiang, L.; Xie, G., Facile synthesis of nanoporous Ni-Fe-P bifunctional catalysts with high performance for overall water splitting. *Journal of Materials Chemistry A* 2019, 7 (6), 2518-2523.
4. (a) Asif, M.; Muneer, T., Energy supply, its demand and security issues for developed and emerging economies. *Renewable and Sustainable Energy Reviews* 2007, 11 (7), 1388-1413; (b) Dagdougui, H., Models, methods and approaches for the planning and design of the future hydrogen supply chain. *International Journal of Hydrogen Energy* 2012, 37 (6), 5318-5327.
5. Tanksale, A.; Beltramini, J. N.; Lu, G. M., A review of catalytic hydrogen production processes from biomass. *Renewable and Sustainable Energy Reviews* 2010, 14 (1), 166-182.
6. Wang, W.; Xu, M.; Xu, X.; Zhou, W.; Shao, Z., Perovskite Oxide Based Electrodes for High-Performance Photoelectrochemical Water Splitting. *Angewandte Chemie International Edition* 2020, 59 (1), 136-152.
7. Li, X.; Hao, X.; Abudula, A.; Guan, G., Nanostructured catalysts for electrochemical water splitting: current state and prospects. *Journal of Materials Chemistry A* 2016, 4 (31), 11973-12000.
8. Gong, Y.; Zhi, Y.; Lin, Y.; Zhou, T.; Li, J.; Jiao, F.; Wang, W., Controlled synthesis of bifunctional particle-like Mo/Mn-Ni₂S₃/NF electrocatalyst for highly efficient overall water splitting. *Dalton Transactions* 2019, 48 (20), 6718-6729.
9. Midilli, A.; Ay, M.; Dincer, I.; Rosen, M. A., On hydrogen and hydrogen energy strategies: I: current status and needs. *Renewable and Sustainable Energy Reviews* 2005, 9 (3), 255-271.

10. Ginde, A. A.; Scragg, R.; Schwartz, R. S.; Camargo Jr., C. A., Prospective Study of Serum 25-Hydroxyvitamin D Level, Cardiovascular Disease Mortality, and All-Cause Mortality in Older U.S. Adults. *Journal of the American Geriatrics Society* 2009, 57 (9), 1595-1603.
11. Zoppi, G.; Forbes, I.; Miles, R. W.; Dale, P. J.; Scragg, J. J.; Peter, L. M., Cu₂ZnSnSe₄ thin film solar cells produced by selenisation of magnetron sputtered precursors. *Progress in Photovoltaics: Research and Applications* 2009, 17 (5), 315-319.
12. Parthasarathy, P.; Narayanan, K. S., Hydrogen production from steam gasification of biomass: Influence of process parameters on hydrogen yield – A review. *Renewable Energy* 2014, 66, 570-579.
13. Wang, J.; Yue, X.; Yang, Y.; Sirisomboonchai, S.; Wang, P.; Ma, X.; Abudula, A.; Guan, G., Earth-abundant transition-metal-based bifunctional catalysts for overall electrochemical water splitting: A review. *Journal of Alloys and Compounds* 2020, 819, 153346.
14. Gregory, D. P.; Rosenberg, R. B., Synthetic Fuels for Transportation and National Energy Needs. *SAE Transactions* 1973, 82, 1676-1684.
15. Tang, Y.-J.; Zhu, H.-J.; Dong, L.-Z.; Zhang, A. M.; Li, S.-L.; Liu, J.; Lan, Y.-Q., Solid-phase hot-pressing of POMs-ZIFs precursor and derived phosphide for overall water splitting. *Applied Catalysis B: Environmental* 2019, 245, 528-535.
16. Zong, Z.; Qian, Z.; Tang, Z.; Liu, Z.; Tian, Y.; Wang, S., Hydrogen evolution and oxygen reduction reactions catalyzed by core-shelled Fe@Ru nanoparticles embedded in porous dodecahedron carbon. *Journal of Alloys and Compounds* 2019, 784, 447-455.
17. Cao, H.; Gong, X.; Liu, T.; Xiao, F.; Lv, X.; Zhou, J.; Gai, L., Hierarchical Co-N microballs with heterostructure exhibiting superior electrochemical properties for water splitting and reduction of I³⁻. *Journal of Alloys and Compounds* 2019, 797, 341-347.
18. (a) Shi, Y.; Zhang, B., Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction. *Chemical Society Reviews* 2016, 45 (6), 1529-1541; (b) Wu, Y.; Li, G.-D.; Liu, Y.; Yang, L.; Lian, X.; Asefa, T.; Zou, X.,
Electrocatalysis: Overall Water Splitting Catalyzed Efficiently by an Ultrathin Nanosheet-Built, Hollow Ni₃S₂-Based Electrocatalyst (*Adv. Funct. Mater.* 27/2016). *Advanced Functional Materials* 2016, 26 (27), 4999-4999; (c) Cheng, Y.; Guo, J.; Huang, Y.; Liao, Z.; Xiang, Z., Ultrastable hydrogen evolution electrocatalyst derived from phosphide postmodified metal-organic frameworks. *Nano Energy* 2017, 35, 115-120.
19. Shiva Kumar, S.; Himabindu, V., Hydrogen production by PEM water electrolysis – A review. *Materials Science for Energy Technologies* 2019, 2 (3), 442-454.
20. Nikolic, V. M.; Tasic, G. S.; Maksic, A. D.; Saponjic, D. P.; Miulovic, S. M.; Marceta Kaninski, M. P., Raising efficiency of hydrogen generation from alkaline water electrolysis – Energy saving. *International Journal of Hydrogen Energy* 2010, 35 (22), 12369-12373.
21. Stojić, D. L.; Grozdić, T. D.; Umićević, B.; Maksić, A. D., A comparison of alkaline and proton exchange membrane electrolyzers. *Russian Journal of Physical Chemistry A, Focus on Chemistry* 2008, 82 (11), 1958.
22. Iwakura, C.; Tanaka, M.; Nakamatsu, S.; Inoue, H.; Matsuoka, M.; Furukawa, N., Electrochemical properties of Ni(Ni + RuO₂) active cathodes for hydrogen evolution in chlor-alkali electrolysis. *Electrochimica Acta* 1995, 40 (8), 977-982.
23. Neagu, C.; Jansen, H.; Gardeniers, H.; Elwenspoek, M., The electrolysis of water: an actuation principle for MEMS with a big opportunity. *Mechatronics* 2000, 10 (4), 571-581.

24. Millet, P.; Andolfatto, F.; Durand, R., Design and performance of a solid polymer electrolyte water electrolyzer. *International Journal of Hydrogen Energy* 1996, 21 (2), 87-93.
25. Stucki, S.; Scherer, G. G.; Schlagowski, S.; Fischer, E., PEM water electrolyzers: evidence for membrane failure in 100kW demonstration plants. *Journal of Applied Electrochemistry* 1998, 28 (10), 1041-1049.
26. Peng, J.; Dong, W.; Wang, Z.; Meng, Y.; Liu, W.; Song, P.; Liu, Z., Recent advances in 2D transition metal compounds for electrocatalytic full water splitting in neutral media. *Materials Today Advances* 2020, 8, 100081.
27. (a) Sijabat, R. R.; de Groot, M. T.; Moshtarihah, S.; van der Schaaf, J., Maxwell-Stefan model of multicomponent ion transport inside a monolayer Nafion membrane for intensified chlor-alkali electrolysis. *Journal of Applied Electrochemistry* 2019, 49 (4), 353-368; (b) Abouatallah, R. M.; Kirk, D. W.; Thorpe, S. J.; Graydon, J. W., Reactivation of nickel cathodes by dissolved vanadium species during hydrogen evolution in alkaline media. *Electrochimica Acta* 2001, 47 (4), 613-621.
28. Hu, W.; Lee, J.-Y., Electrocatalytic properties of Ti₂Ni/Ni-Mo composite electrodes for hydrogen evolution reaction. *International Journal of Hydrogen Energy* 1998, 23 (4), 253-257.
29. Hu, W., Electrocatalytic properties of new electrocatalysts for hydrogen evolution in alkaline water electrolysis. *International Journal of Hydrogen Energy* 2000, 25 (2), 111-118.
30. Sheela, G.; Pushpavanam, M.; Pushpavanam, S., Zinc-nickel alloy electrodeposits for water electrolysis. *International Journal of Hydrogen Energy* 2002, 27 (6), 627-633.
31. Tavares, A. C.; Trasatti, S., Ni+RuO₂ co-deposited electrodes for hydrogen evolution. *Electrochimica Acta* 2000, 45 (25), 4195-4202.
32. Liu, Q.; Wang, E.; Sun, G., Layered transition-metal hydroxides for alkaline hydrogen evolution reaction. *Chinese Journal of Catalysis* 2020, 41 (4), 574-591.
33. Faber, M. S.; Jin, S., Earth-abundant inorganic electrocatalysts and their nanostructures for energy conversion applications. *Energy & Environmental Science* 2014, 7 (11), 3519-3542.
34. Tang, B.; Yu, Z. G.; Zhang, Y.; Tang, C.; Seng, H. L.; Seh, Z. W.; Zhang, Y.-W.; Pennycook, S. J.; Gong, H.; Yang, W., Metal-organic framework-derived hierarchical MoS₂/CoS₂ nanotube arrays as pH-universal electrocatalysts for efficient hydrogen evolution. *Journal of Materials Chemistry A* 2019, 7 (21), 13339-13346.
35. Xie, L.; Zhang, R.; Cui, L.; Liu, D.; Hao, S.; Ma, Y.; Du, G.; Asiri, A. M.; Sun, X., High-Performance Electrolytic Oxygen Evolution in Neutral Media Catalyzed by a Cobalt Phosphate Nanoarray. *Angewandte Chemie International Edition* 2017, 56 (4), 1064-1068.
36. Qin, C.; Fan, A.; Zhang, X.; Wang, S.; Yuan, X.; Dai, X., Interface engineering: few-layer MoS₂ coupled to a NiCo-sulfide nanosheet heterostructure as a bifunctional electrocatalyst for overall water splitting. *Journal of Materials Chemistry A* 2019, 7 (48), 27594-27602.
37. Spanos, I.; Tesch, M. F.; Yu, M.; Tüysüz, H.; Zhang, J.; Feng, X.; Müllen, K.; Schlögl, R.; Mechler, A. K., Facile Protocol for Alkaline Electrolyte Purification and Its Influence on a Ni-Co Oxide Catalyst for the Oxygen Evolution Reaction. *ACS Catalysis* 2019, 9 (9), 8165-8170.

- 38.(a) Sun, T.; Zhang, G.; Xu, D.; Lian, X.; Li, H.; Chen, W.; Su, C., Defect chemistry in 2D materials for electrocatalysis. *Materials Today Energy* 2019, 12, 215-238; (b) Li, R.; Li, X.; Yu, D.; Li, L.; Yang, G.; Zhang, K.; Ramakrishna, S.; Xie, L.; Peng, S., Ni₃ZnCo_{0.7} nanodots decorating nitrogen-doped carbon nanotube arrays as a self-standing bifunctional electrocatalyst for water splitting. *Carbon* 2019, 148, 496-503.
- 39.Sung, M.-C.; Lee, G.-H.; Kim, D.-W., CeO₂/Co(OH)₂ hybrid electrocatalysts for efficient hydrogen and oxygen evolution reaction. *Journal of Alloys and Compounds* 2019, 800, 450-455.
- 40.Jamesh, M. L., Recent progress on earth abundant hydrogen evolution reaction and oxygen evolution reaction bifunctional electrocatalyst for overall water splitting in alkaline media. *Journal of Power Sources* 2016, 333, 213-236.
- 41.Liang, J.; Ma, F.; Hwang, S.; Wang, X.; Sokolowski, J.; Li, Q.; Wu, G.; Su, D., Atomic Arrangement Engineering of Metallic Nanocrystals for Energy-Conversion Electrocatalysis. *Joule* 2019, 3 (4), 956-991.
- 42.Li, T.; Li, S.; Liu, Q.; Yin, J.; Sun, D.; Zhang, M.; Xu, L.; Tang, Y.; Zhang, Y., Immobilization of Ni₃Co Nanoparticles into N-Doped Carbon Nanotube/Nanofiber Integrated Hierarchically Branched Architectures toward Efficient Overall Water Splitting. *Advanced Science* 2020, 7 (1), 1902371.
- 43.(a) Jia, X.; Zhao, Y.; Chen, G.; Shang, L.; Shi, R.; Kang, X.; Waterhouse, G. I. N.; Wu, L.-Z.; Tung, C.-H.; Zhang, T., Ni₃FeN Nanoparticles Derived from Ultrathin NiFe-Layered Double Hydroxide Nanosheets: An Efficient Overall Water Splitting Electrocatalyst. *Advanced Energy Materials* 2016, 6 (10), 1502585; (b) Yin, Y.; Zhang, Y.; Gao, T.; Yao, T.; Zhang, X.; Han, J.; Wang, X.; Zhang, Z.; Xu, P.; Zhang, P.; Cao, X.; Song, B.; Jin, S., Synergistic Phase and Disorder Engineering in 1T-MoSe₂ Nanosheets for Enhanced Hydrogen-Evolution Reaction. *Advanced Materials* 2017, 29 (28), 1700311.
- 44.Fu, Q.; Wu, T.; Fu, G.; Gao, T.; Han, J.; Yao, T.; Zhang, Y.; Zhong, W.; Wang, X.; Song, B., Skutterudite-Type Ternary Co_{1-x}Ni_xP₃ Nanoneedle Array Electrocatalysts for Enhanced Hydrogen and Oxygen Evolution. *ACS Energy Letters* 2018, 3 (7), 1744-1752.
- 45.Yang, Y.; Luo, M.; Xing, Y.; Wang, S.; Zhang, W.; Lv, F.; Li, Y.; Zhang, Y.; Wang, W.; Guo, S., A Universal Strategy for Intimately Coupled Carbon Nanosheets/MoM Nanocrystals (M = P, S, C, and O) Hierarchical Hollow Nanospheres for Hydrogen Evolution Catalysis and Sodium-Ion Storage. *Advanced Materials* 2018, 30 (18), 1706085.
- 46.Zhou, G.; Li, M.; Li, Y.; Dong, H.; Sun, D.; Liu, X.; Xu, L.; Tian, Z.; Tang, Y., Regulating the Electronic Structure of CoP Nanosheets by O Incorporation for High-Efficiency Electrochemical Overall Water Splitting. *Advanced Functional Materials* 2020, 30 (7), 1905252.
- 47.Wang, H. B.; Wang, H.; Wang, X. N.; Zhang, J.; Wu, S.; Duan, J. X.; Jiang, Y., Organic co-decomposition method for the synthesis of Mn and Co doped ZnO submicrometer crystals: Photoluminescence and magnetic properties. *physica status solidi (a)* 2011, 208 (10), 2393-2398.
- 48.Zhang, T.; Dong, W.; Keeter-Brewer, M.; Konar, S.; Njabon, R. N.; Tian, Z. R., Site-Specific Nucleation and Growth Kinetics in Hierarchical Nanosyntheses of Branched ZnO Crystallites. *Journal of the American Chemical Society* 2006, 128 (33), 10960-10968.
- 49.Wang, Z.; Gong, J.; Su, Y.; Jiang, Y.; Yang, S., Six-Fold-Symmetrical Hierarchical ZnO Nanostructure Arrays: Synthesis, Characterization, and Field Emission Properties. *Crystal Growth & Design* 2010, 10 (6), 2455-2459.

- 50.Liu, L.; Tan, X.; Teng, D.; Wu, M.; Wang, G., Simultaneously Enhancing the Angular-Color Uniformity, Luminous Efficiency, and Reliability of White Light-Emitting Diodes by ZnO@SiO₂ Modified Silicones. *IEEE Transactions on Components, Packaging and Manufacturing Technology* 2015, 5 (5), 599-605.
- 51.Bagnall, D. M.; Chen, Y. F.; Zhu, Z.; Yao, T.; Koyama, S.; Shen, M. Y.; Goto, T., Optically pumped lasing of ZnO at room temperature. *Applied Physics Letters* 1997, 70 (17), 2230-2232.
- 52.Gimenez, A. J.; Yáñez-Limón, J. M.; Seminario, J. M., ZnO-Paper Based Photoconductive UV Sensor. *The Journal of Physical Chemistry C* 2011, 115 (1), 282-287.
- 53.Gupta, T. K., Application of Zinc Oxide Varistors. *Journal of the American Ceramic Society* 1990, 73 (7), 1817-1840.
- 54.Goldberger, J.; Sirbully, D. J.; Law, M.; Yang, P., ZnO Nanowire Transistors. *The Journal of Physical Chemistry B* 2005, 109 (1), 9-14.
- 55.Park, S.-E.; Shrout, T. R., Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. *Journal of Applied Physics* 1997, 82 (4), 1804-1811.
- 56.Zhou, Q. F.; Sharp, C.; Cannata, J. M.; Shung, K. K.; Feng, G. H.; Kim, E. S., Self-focused high frequency ultrasonic transducers based on ZnO piezoelectric films. *Applied Physics Letters* 2007, 90 (11), 113502.
- 57.Kim, H. C.; Song, S.; Kim, J., Fabrication of a Miniaturized ZnO Nanowire Accelerometer and Its Performance Tests. *Sensors* 2016, 16 (9), 1499.
- 58.Li, X.; Wang, C.; Guo, H.; Sun, P.; Liu, F.; Liang, X.; Lu, G., Double-Shell Architectures of ZnFe₂O₄ Nanosheets on ZnO Hollow Spheres for High-Performance Gas Sensors. *ACS Applied Materials & Interfaces* 2015, 7 (32), 17811-17818.
- 59.Shi, L.; Naik, A. J. T.; Goodall, J. B. M.; Tighe, C.; Gruar, R.; Binions, R.; Parkin, I.; Darr, J., Highly Sensitive ZnO Nanorod- and Nanoprism-Based NO₂ Gas Sensors: Size and Shape Control Using a Continuous Hydrothermal Pilot Plant. *Langmuir* 2013, 29 (33), 10603-10609.
- 60.Vaishampayan, M. V.; Mulla, I. S.; Joshi, S. S., Optical and Photocatalytic Properties of Single Crystalline ZnO at the Air-Liquid Interface by an Aminolytic Reaction. *Langmuir* 2011, 27 (20), 12751-12759.
- 61.Norris, B. J.; Anderson, J.; Wager, J. F.; Keszler, D. A., Spin-coated zinc oxide transparent transistors. *Journal of Physics D: Applied Physics* 2003, 36 (20), L105-L107.
- 62.Sun, Y.; Wen, D., Conductance Quantization in Nonvolatile Resistive Switching Memory Based on the Polymer Composite of Zinc Oxide Nanoparticles. *The Journal of Physical Chemistry C* 2018, 122 (19), 10582-10591.
- 63.Céspedes, E.; Laguna-Marco, M. A.; Jiménez-Villacorta, F.; Chaboy, J.; Boada, R.; Guglieri, C.; Andrés, A. d.; Prieto, C., On the Origin of the Magnetism of Mn-Zn-O Systems: Structural, Electronic, and Magnetic Study of Exotic MnO₂-δ/ZnO Thin Films. *The Journal of Physical Chemistry C* 2011, 115 (49), 24092-24101.
- 64.Singh, P.; Kumar, R.; Singh, R. K., Progress on Transition Metal-Doped ZnO Nanoparticles and Its Application. *Industrial & Engineering Chemistry Research* 2019, 58 (37), 17130-17163.
- 65.Wang, Y.; Yang, Y.; Zhang, X.; Liu, X.; Nakamura, A., Optical investigation on cadmium-doped zinc oxide nanoparticles synthesized by using a sonochemical method. *CrystEngComm* 2012, 14 (1), 240-245.
- 66.Mandal, S. K.; Das, A. K.; Nath, T. K.; Karmakar, D., Temperature dependence of solubility limits of transition metals (Co, Mn, Fe, and Ni) in ZnO nanoparticles. *Applied Physics Letters* 2006, 89 (14), 144105.

- 67.Djerdj, I.; Garnweitner, G.; Arčon, D.; Pregelj, M.; Jagličić, Z.; Niederberger, M., Diluted magnetic semiconductors: Mn/Co-doped ZnO nanorods as case study. *Journal of Materials Chemistry* 2008, 18 (43), 5208-5217.
- 68.Ki. K. J.; Park, Y. R., Spectroscopic ellipsometry study of optical transitions in $Zn_{1-x}Co_xO$ alloys. *Applied Physics Letters* 2002, 81 (8), 1420-1422.
- 69.Pearnton, S. J.; Norton, D. P.; Ivill, M. P.; Hebard, A. F.; Zavada, J. M.; Chen, W. M.; Buyanova, I. A., ZnO Doped With Transition Metal Ions. *IEEE Transactions on Electron Devices* 2007, 54 (5), 1040-1048.
- 70.Nath, S. K.; Chowdhury, N.; Gafur, M. A., Effect of Co Doping on Crystallographic and Optoelectronic Properties of ZnO Thin Films. *Journal of Superconductivity and Novel Magnetism* 2015, 28 (1), 117-123.
- 71.Tiwari, A.; Jin, C.; Kvit, A.; Kumar, D.; Muth, J. F.; Narayan, J., Structural, optical and magnetic properties of diluted magnetic semiconducting $Zn_{1-x}Mn_xO$ films. *Solid State Communications* 2002, 121 (6), 371-374.
- 72.Wu, D.; Huang, Z.; Yin, G.; Yao, Y.; Liao, X.; Han, D.; Huang, X.; Gu, J., Preparation, structure and properties of Mn-doped ZnO rod arrays. *CrystEngComm* 2010, 12 (1), 192-198.
- 73.Phan, T.-L.; Yu, S. C., Optical and Magnetic Properties of $Zn_{1-x}Mn_xO$ Nanorods Grown by Chemical Vapor Deposition. *The Journal of Physical Chemistry C* 2013, 117 (12), 6443-6453.
- 74.Maier, W.; Arlt, T.; Wannek, C.; Manke, I.; Riesemeier, H.; Krüger, P.; Scholta, J.; Lehnert, W.; Banhart, J.; Stolten, D., In-situ synchrotron X-ray radiography on high temperature polymer electrolyte fuel cells. *Electrochemistry Communications* 2010, 12 (10), 1436-1438.
- 75.Kreuter, W.; Hofmann, H., Electrolysis: The important energy transformer in a world of sustainable energy. *International Journal of Hydrogen Energy* 1998, 23 (8), 661-666.
- 76.Bockris, J. O. M.; Potter, E. C., The Mechanism of the Cathodic Hydrogen Evolution Reaction. *Journal of The Electrochemical Society* 1952, 99 (4), 169.
- 77.Funk, J. E.; Thorpe, J. F., Void Fraction and Current Density Distributions in a Water Electrolysis Cell. *Journal of The Electrochemical Society* 1969, 116 (1), 48.
- 78.Zeng, K.; Zhang, D., Recent progress in alkaline water electrolysis for hydrogen production and applications. *Progress in Energy and Combustion Science* 2010, 36 (3), 307-326.
- 79.Wrighton, M. S.; Ginley, D. S.; Wolczanski, P. T.; Ellis, A. B.; Morse, D. L.; Linz, A., Photoassisted Electrolysis of Water by Irradiation of a Titanium Dioxide Electrode. *Proceedings of the National Academy of Sciences* 1975, 72 (4), 1518-1522.
- 80.Miles, M. H.; Thomason, M. A., Periodic Variations of Overvoltages for Water Electrolysis in Acid Solutions from Cyclic Voltammetric Studies. *Journal of The Electrochemical Society* 2019, 123 (10), 1459-1461.
- 81.Ibl, N.; Puippe, J. C.; Angerer, H., Electrocrystallization in pulse electrolysis. *Surface Technology* 1978, 6 (4), 287-300.
- 82.Doenitz, W.; Schmidberger, R.; Steinheil, E.; Streicher, R., Hydrogen production by high temperature electrolysis of water vapour. *International Journal of Hydrogen Energy* 1980, 5 (1), 55-63.
- 83.Iwahara, H.; Esaka, T.; Uchida, H.; Maeda, N., Proton conduction in sintered oxides and its application to steam electrolysis for hydrogen production. *Solid State Ionics* 1981, 3-4, 359-363.
- 84.He, T.; Kar, M.; McDaniel, N. D.; Randolph, B. B., Electrochemical Hydrogen Production. In *Springer Handbook of Electrochemical Energy*, Breitkopf, C.; Swider-Lyons, K., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 2017; pp 897-940.

85. Botte, G. G.; Muthuvel, M., Electrochemical Energy Storage: Applications, Processes, and Trends. In Handbook of Industrial Chemistry and Biotechnology, Kent, J. A., Ed. Springer US: Boston, MA, 2012; pp 1497-1539.
86. Kamida, K.; Okajima, K.; Matsui, T.; Kowsaka, K., Study on the Solubility of Cellulose in Aqueous Alkali Solution by Deuteration IR and ¹³C NMR. Polymer Journal 1984, 16 (12), 857-866.
87. Phillips, R.; Edwards, A.; Rome, B.; Jones, D. R.; Dunnill, C. W., Minimising the ohmic resistance of an alkaline electrolysis cell through effective cell design. International Journal of Hydrogen Energy 2017, 42 (38), 23986-23994.
88. Dukovic, J.; Tobias, C. W., The Influence of Attached Bubbles on Potential Drop and Current Distribution at Gas-Evolving Electrodes. Journal of The Electrochemical Society 2019, 134 (2), 331-343.
89. Nagai, N.; Takeuchi, M.; Kimura, T.; Oka, T., Existence of optimum space between electrodes on hydrogen production by water electrolysis. International Journal of Hydrogen Energy 2003, 28 (1), 35-41.
90. Czarnetzki, L. R.; Janssen, L. J. J., Electrode current distribution in a hypochlorite cell. Journal of Applied Electrochemistry 1989, 19 (5), 630-636.
91. Balej, J., Determination of the oxygen and hydrogen overvoltage in concentrated alkali hydroxide solutions. International Journal of Hydrogen Energy 1985, 10 (6), 365-374.
92. Morimoto, T.; Yoshitake, M.; Morikawa, S.; Oda, Y., Alkaline type ion-exchange membrane water electrolysis. International Journal of Hydrogen Energy 1986, 11 (8), 503-506.
93. Matsumoto, Y.; Sato, E., Electrocatalytic properties of transition metal oxides for oxygen evolution reaction. Materials Chemistry and Physics 1986, 14 (5), 397-426.
94. Wendt, H.; Hofmann, H.; Plzak, V., Materials research and development of electrocatalysts for alkaline water electrolysis. Materials Chemistry and Physics 1989, 22 (1), 27-49.
95. Wendt, H.; Hofmann, H., Ceramic diaphragms for advanced alkaline water electrolysis. Journal of Applied Electrochemistry 1989, 19 (4), 605-610.
96. Xia, Y.; Yang, Y.; Shao, H., Activation behaviour of the Ni/MH batteries electrodic material Ni(OH)₂ by single particle microelectrode technique. International Journal of Hydrogen Energy 2011, 36 (14), 8560-8569.
97. Hine, F., Gas Void Fraction in Electrolytic Cell. Soda to Enso 1980, 31, 347-362.
98. Nishiki, Y.; Aoki, K.; Tokuda, K.; matsuda, H., Effect of gas evolution on current distribution and ohmic resistance in a vertical cell under forced convection conditions. Journal of Applied Electrochemistry 1986, 16 (4), 615-625.
99. St-Pierre, J.; Wragg, A. A., Behaviour of electrogenerated hydrogen and oxygen bubbles in narrow gap cells—Part I. Experimental. Electrochimica Acta 1993, 38 (10), 1381-1390.
100. Fournier, J.; Wrona, P. K.; Lasia, A.; Lacasse, R.; Lalancette, J. M.; Menard, H.; Brossard, L., Catalytic Influence of Commercial Ru, Rh, Pt, and Pd (~0,1 atomic percent) Intercalated in Graphite on the Hydrogen Evolution Reaction. Journal of The Electrochemical Society 2019, 139 (9), 2372-2378.
101. Garcia-Conde, A. G.; Rosa, F., Solar hydrogen production: A spanish experience. International Journal of Hydrogen Energy 1993, 18 (12), 995-1000.
102. Divisek, J.; Schmitz, H.; Steffen, B., Electrocatalyst materials for hydrogen evolution.

- Electrochimica Acta 1994, 39 (11), 1723-1731.
103. Terenzi, C.; Bouguet-Bonnet, S.; Canet, D., Electron Spin Polarization Transfer to ortho-H₂ by Interaction of para-H₂ with Paramagnetic Species: A Key to a Novel para → ortho Conversion Mechanism. The Journal of Physical Chemistry Letters 2015, 6 (9), 1611-1615.
 104. Valiev, R. R.; Minaev, B. F., Influence of Molecular Oxygen on Ortho-Para Conversion of Water Molecules. Russian Physics Journal 2017, 60 (3), 485-493.
 105. El-Deab, M. S.; El-Shakre, M. E.; El-Anadoul, B. E.; Ateya, B. G., Hydrogen evolution on stacked copper screen electrodes from flowing alkaline solutions. International Journal of Hydrogen Energy 1996, 21 (4), 273-280.
 106. Abdelouahed, L.; Valentin, G.; Poncin, S.; Lapique, F., Current density distribution and gas volume fraction in the gap of lantern blade electrodes. Chemical Engineering Research and Design 2014, 92 (3), 559-570.
 107. Hung, C.-Y.; Li, S.-D.; Wang, C.-C.; Chen, C.-Y., Influences of a bipolar membrane and an ultrasonic field on alkaline water electrolysis. Journal of Membrane Science 2012, 389, 197-204.
 108. Hu, W.; Cao, X.; Wang, F.; Zhang, Y., A novel cathode for alkaline water electrolysis. International Journal of Hydrogen Energy 1997, 22 (6), 621-623.
 109. Riegel, H.; Mitrovic, J.; Stephan, K., Role of mass transfer on hydrogen evolution in aqueous media. Journal of Applied Electrochemistry 1998, 28 (1), 10-17.
 110. Ikeda, S.; Tanaka, A.; Hosono, H.; Kawazoe, H.; Hara, M.; Kondo, J. N.; Domen, K., Overall water splitting on Cu(I)-containing ternary oxides, CuMO₂(M=Fe, Ga, Al) with delafossite structure. In Studies in Surface Science and Catalysis, Hattori, H.; Otsuka, K., Eds. Elsevier: 1999; Vol. 121, pp 301-304.
 111. Meguro, S.; Sasaki, T.; Katagiri, H.; Habazaki, H.; Kawashima, A.; Sakaki, T.; Asami, K.; Hashimoto, K., Electrodeposited Ni-Fe-C Cathodes for Hydrogen Evolution. Journal of The Electrochemical Society 2000, 147 (8), 3003.
 112. Marshall, A. T.; Haverkamp, R. G., Production of hydrogen by the electrochemical reforming of glycerol-water solutions in a PEM electrolysis cell. International Journal of Hydrogen Energy 2008, 33 (17), 4649-4654.
 113. Boggs, B. K.; King, R. L.; Botte, G. G., Urea electrolysis: direct hydrogen production from urine. Chemical Communications 2009, (32), 4859-4861.
 114. Miltner, A.; Wukovits, W.; Pröll, T.; Friedl, A., Renewable hydrogen production: a technical evaluation based on process simulation. Journal of Cleaner Production 2010, 18, S51-S62.
 115. Li, H.; Qin, X.; Zhang, W.; Pan, W., Synthesis of Co-Doped ZnO Nanofibers and Their Magnetic Properties. Journal of the American Ceramic Society 2012, 95 (1), 217-222.
 116. Mazloomi, K.; Gomes, C., Hydrogen as an energy carrier: Prospects and challenges. Renewable and Sustainable Energy Reviews 2012, 16 (5), 3024-3033.
 117. Dolcet, P.; Latini, F.; Casarin, M.; Speghini, A.; Tondello, E.; Foss, C.; Diodati, S.; Verin, L.; Motta, A.; Gross, S., Inorganic Chemistry in a Nanoreactor: Doped ZnO Nanostructures by Miniemulsion. European Journal of Inorganic Chemistry 2013, 2013 (13), 2291-2300.
 118. Yang, Y.; Fei, H.; Ruan, G.; Tour, J. M., Porous Cobalt-Based Thin Film as a Bifunctional Catalyst for Hydrogen Generation and Oxygen Generation. Advanced Materials 2015, 27 (20), 3175-3180.
 119. Kamarulzaman, N.; Kasim, M. F.; Rusdi, R., Band Gap Narrowing and Widening of ZnO Nanostructures and Doped Materials. Nanoscale Research Letters 2015, 10 (1), 346.

120. Zhukovskii, Y. F.; Piskunov, S.; Lisovski, O.; Bocharov, D.; Evarestov, R. A., Doped 1D Nanostructures of Transition-metal Oxides: First-principles Evaluation of Photocatalytic Suitability. *Israel Journal of Chemistry* 2017, 57 (6), 461-476.
121. Wang, D.; Astruc, D., The recent development of efficient Earth-abundant transition-metal nanocatalysts. *Chemical Society Reviews* 2017, 46 (3), 816-854.
122. Ambrosi, A.; Pumera, M., Self-Contained Polymer/Metal 3D Printed Electrochemical Platform for Tailored Water Splitting. *Advanced Functional Materials* 2018, 28 (27), 1700655.
123. Tee, S. Y.; Win, K. Y.; Teo, W. S.; Koh, L.-D.; Liu, S.; Teng, C. P.; Han, M.-Y., Recent Progress in Energy-Driven Water Splitting. *Advanced Science* 2017, 4 (5), 1600337.
124. Wang, S.; He, T.; Yun, J.-H.; Hu, Y.; Xiao, M.; Du, A.; Wang, L., New Iron-Cobalt Oxide Catalysts Promoting BiVO₄ Films for Photoelectrochemical Water Splitting. *Advanced Functional Materials* 2018, 28 (34), 1802685.
125. Lucci, I.; Charbonnier, S.; Vallet, M.; Turban, P.; Léger, Y.; Rohel, T.; Bertru, N.; Létoublon, A.; Rodriguez, J.-B.; Cerutti, L.; Tournié, E.; Ponchet, A.; Patriarche, G.; Pedesseau, L.; Cornet, C., A Stress-Free and Textured GaP Template on Silicon for Solar Water Splitting. *Advanced Functional Materials* 2018, 28 (30), 1801585.
126. Yao, T.; An, X.; Han, H.; Chen, J. Q.; Li, C., Photoelectrocatalytic Materials for Solar Water Splitting. *Advanced Energy Materials* 2018, 8 (21), 1800210.
127. Zhang, Q.; He, B.; Tang, L.; Zhou, Z.; Kang, L.; Sun, J.; Zhang, T.; Li, Q.; Li, C.; Zhao, J.; Zhang, Z.; Wei, L.; Yao, Y., Fully Solar-Powered Uninterrupted Overall Water-Splitting Systems. *Advanced Functional Materials* 2019, 29 (9), 1808889.
128. Hou, J.; Wu, Y.; Zhang, B.; Cao, S.; Li, Z.; Sun, L., Rational Design of Nanoarray Architectures for Electrocatalytic Water Splitting. *Advanced Functional Materials* 2019, 29 (20), 1808367.
129. Li, Y.; Tsang, S. C. E., Recent progress and strategies for enhancing photocatalytic water splitting. *Materials Today Sustainability* 2020, 9, 100032.
130. Fu, Q.; Han, J.; Wang, X.; Xu, P.; Yao, T.; Zhong, J.; Zhong, W.; Liu, S.; Gao, T.; Zhang, Z.; Xu, L.; Song, B., 2D Transition Metal Dichalcogenides: Design, Modulation, and Challenges in Electrocatalysis. *Advanced Materials* n/a (n/a), 1907818.
131. Zhang, H.; Maijenburg, A. W.; Li, X.; Schweizer, S. L.; Wehrspohn, R. B., Bifunctional Heterostructured Transition Metal Phosphides for Efficient Electrochemical Water Splitting. *Advanced Functional Materials* 2020, 30 (34), 2003261.
132. Lin, J.; Wang, W.; Li, G., Modulating Surface/Interface Structure of Emerging InGaN Nanowires for Efficient Photoelectrochemical Water Splitting. *Advanced Functional Materials* n/a (n/a), 2005677.
133. Lv, X.; Li, X.; Yang, C.; Ding, X.; Zhang, Y.; Zheng, Y.-Z.; Li, S.; Sun, X.; Tao, X., Large-Size, Porous, Ultrathin NiCoP Nanosheets for Efficient Electro/Photocatalytic Water Splitting. *Advanced Functional Materials* 2020, 30 (16), 1910830.
134. ZnO Nanostructures for Photocatalytic Dye Degradation Under Visible Light Irradiation. In *Environmental Nanotechnology for Water Purification*, 2020; pp 259-284.
135. Ng, B.-J.; Putri, L. K.; Kong, X. Y.; Teh, Y. W.; Pasbakhsh, P.; Chai, S.-P., Z-Scheme Photocatalytic Systems for Solar Water Splitting. *Advanced Science* 2020, 7 (7), 1903171.
136. Yadav, H. K.; Sreenivas, K.; Gupta, V., Influence of postdeposition annealing on the structural and optical properties of co-sputtered Mn doped ZnO thin films. *Journal of Applied Physics* 2006, 99 (8), 083507.

137. Joo, J.; Kwon, S. G.; Yu, J. H.; Hyeon, T., Synthesis of ZnO Nanocrystals with Cone, Hexagonal Cone, and Rod Shapes via Non-Hydrolytic Ester Elimination Sol-Gel Reactions. *Advanced Materials* 2005, 17 (15), 1873-1877.
138. Lee, H.-J.; Jeong, S.-Y.; Cho, C. R.; Park, C. H., Study of diluted magnetic semiconductor: Co-doped ZnO. *Applied Physics Letters* 2002, 81 (21), 4020-4022.
139. Clavel, G.; Willinger, M.-G.; Zitoun, D.; Pinna, N., Solvent Dependent Shape and Magnetic Properties of Doped ZnO Nanostructures. *Advanced Functional Materials* 2007, 17 (16), 3159-3169.
140. Fukumura, T.; Jin, Z.; Ohtomo, A.; Koinuma, H.; Kawasaki, M., An oxide-diluted magnetic semiconductor: Mn-doped ZnO. *Applied Physics Letters* 1999, 75 (21), 3366-3368.

