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# COPPER DOPED METAL OXYCHLORIDE (CU-MOCL) FOR HYDROGEN PRODUCTION

**Shahid Munir[*1], Muhammad Muzammil[2], Iqra Noreen[3], Dr Muhammad Altaf[4]**

[*1,4]*Department of Chemistry, Lahore Garrison University*
[2]*Department of Chemistry, Govt. College University Lahore*
[3]*Department of Chemistry, Government College University Faisalabad, Pakistan*

[*1]shahidmunir722@gmail.com

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**Corresponding Author:** *
**Shahid Munir**

**Abstract**
*Copper doped metal oxychlorides are typically produced through reaction of copper metal with hydrochloric acid in the presence of oxygen or by oxidizing copper chloride. Hydrogen can be produced through different methods. Hydrogen production also assisted through the emerging technologies that makes them enable for high quality. The industries providing almost half of the hydrogen produced worldwide. It is produced through heating the gas while nickel is used a catalyst for accelerate the production. The photocatalytic hydrogen production can be improved through precious metals such as Au, Ru, Pt, Pd. Copper-doped metal oxychloride has gained special attention for effective the hydrogen production. The improvement in hydrogen generation shown by loading of different metal doping nanocomposite materials with copper doped metal oxychloride. Recent research has focused a lot of attention on copper-doped metal oxychloride and its application in the hydrogen evolution process due to its emerging properties. This manuscript describes the use of copper-doped metal oxychloride (Cu-MOCl) for hydrogen production.*

## 1. INTRODUCTION

Copper doped metal oxychloride is typically produced by reacting the copper metal with hydrochloric acid in the presence of oxygen or oxidizing copper chloride [1]. Usually, they are also produced reacting hydrochloric acid with copper metal or by air oxidizing solutions of cuprous chloride. They can be produced by aerating copper in an acidic sodium chloride solution. A strong copper chloride solution can also be neutralized to produce them [2,3].

Hydrogen may be produced through different methods. Some methods have shortcomings that make them inefficient for industrial significance. Hydrogen production also assisted through the emerging technologies that makes them enable for high quality. These processes produced the carbon monoxide [4,5]. Therefore, in a following phase, CO is largely converted into carbon dioxide (CO2) in one or more chemical reactors using the water-gas shift (WGS) and preferential oxidation (PrOx) or methanation processes. Green hydrogen production based on renewable energy, blue that based on natural gas and coal gasification, as well as CCS hydrogen generating systems[6,7].

Previous literature reported that different metals could be used for production of hydrogen. These are copper, cerium, iron, and copper [8]. However, the production has be influenced through various factors such as material availability and abundance, simplicity, chemical viability, thermodynamic feasibility, and safety considerations. Nonetheless, most of the hydrogen production need process heat at temperatures over 800 °C.

Although the bulk of green hydrogen is produced using the CO2-intensive steam methane reforming the process. The green hydrogen may also be produced using renewable energy sources. One common technique for producing the green hydrogen without directly releasing the carbon dioxide is electrolysis, which splits the water into hydrogen and oxygen using an electrical current. The required electricity might be generated from the renewable energy sources [5,6,7].

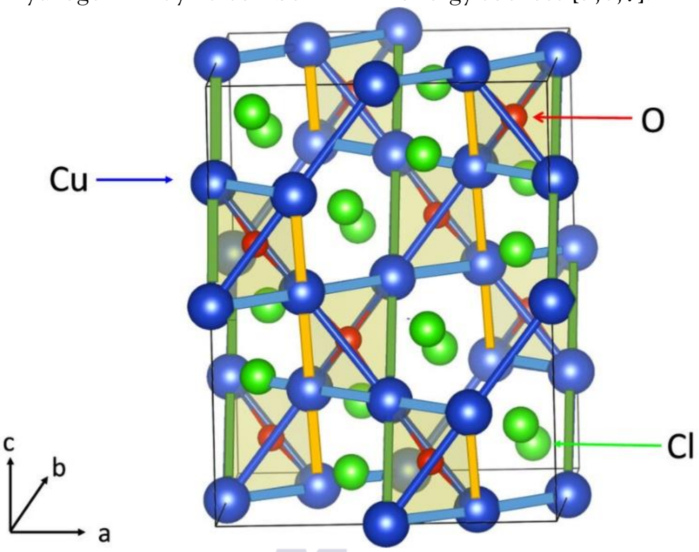

**Fig-1:Shows the structural features of copper doped metal oxychloride**

The hydrogen production through utilization of various metals required the costs [7, 8]. Electrolysis cost is about twice as much to manufacture using 5 cents/kWh of energy as natural gas-based hydrogen. The natural gas pipeline system may be able to transport the less hydrogen in addition to assisting in lowering the CO2 emissions from the existing natural gas reforming facilities [8,9].

This manuscript describes how copper-doped metal oxychloride (Cu-MOCl) is used to for hydrogen production.

**Limitations of different methods for hydrogen production**

The conventional methods for production of hydrogen are employed to fulfil the worldwide need, which is now being satisfied by renewable energy sources [9,10]. These processes also provide the substantial quantity of the hydrogen. The majority of conventional hydrogen is produced from fossil fuels, mostly by the reformation of the natural gas and the partial oxidation of methane. Desulfurization, that removes the gaseous hydrogen sulphide (H2S) and is found in raw natural gas. The Claus procedure is utilized to recover the sulphur from gaseous H2S. Sulphur is eliminated by the reaction of oxygen gas with gaseous hydrogen sulphide generated in Claus plants [11,12].

Three methods such as pressure swing adsorption, membrane separation, or cryogenic air separation are used to separate the air. Coal pyrolysis comes after the air separation process. Two inputs are needed for the pyrolysis stage of coal gasification[13,14]. Char and volatiles are produced when coal is broken down using this process. The quick cooling process known as quenching. The next step is a syngas cooling unit, which captures the heat for syngas, which may be used to heat areas, provide hot water, and create electricity, among other uses.

Prior to the water gas shift operation, the syngas chilling unit converts the carbon dioxide (CO) into the CO2 and separates the hydrogen sulphide (H2S). Following the hydrogen purification unit, the acid gas removal step frequently uses the fine pressure to separate the hydrogen from other gases[11,13]. The industrial process of steam reforming (SMR), which creates the hydrogen, uses natural gas. In general, carbon dioxide, often known as grey hydrogen, is a

greenhouse gas produced by steam reforming. The hydrogen is produced when carbon dioxide is caught and retained is known as blue hydrogen.
Steam methane reformation (SMR) produces the hydrogen from natural gas, mostly methane ($CH_4$), and water [14,15]. It is the most economical source of industrial hydrogen, providing almost half of the hydrogen produced worldwide. The resulting endothermic reaction generates carbon monoxide and molecular hydrogen ($H_2$). The water-gas shift method creates more $H_2$ by combining steam and carbon monoxide. Depending on the quality of the fuel, one ton of hydrogen will also produce nine to twelve tons of $CO_2$, a collectable greenhouse gas [16,17].

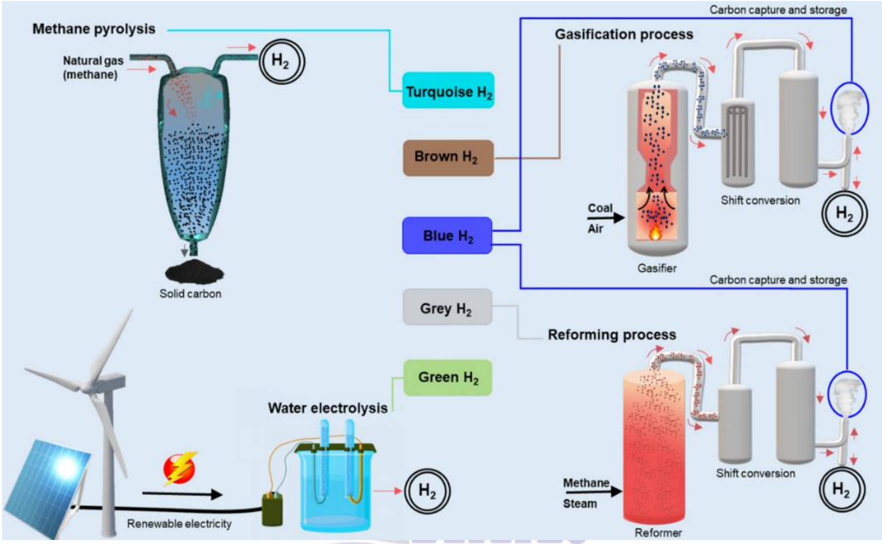


**Fig-2: Shows the production of hydrogen through different methods**



One method for producing the hydrogen without the use of fossil fuels is water splitting, which is the process of dividing the water molecule into hydrogen and oxygen. The phrase "green hydrogen" refers to the hydrogen produced when water splitting is powered by a low-carbon or renewable energy source. There several ways to accomplish the conversion, all of them are currently more expensive than the fossil fuel-based manufacturing techniques [14,16].
However, the most successful water electrolysis methods in the market have an effective electrical efficiency of 70–80%, which means that 1 kilogram of hydrogen, with a specific energy of 143 MJ/kg, or around 40 kWh/kg, requires 50–55 kWh of electricity to create [11,15]. Natural gas and heavier hydrocarbons can be converted to hydrogen by the partial oxidation. The syngas produced by burning a fuel-air or fuel-oxygen mixture is high in carbon monoxide and hydrogen. Carbon monoxide together with water is subsequently transformed into additional hydrogen by the water-gas shift mechanism. Co-feeding carbon dioxide to carbon monoxide ratio can lower the hydrogen. The partial oxidation process occurs in a reformer or partial oxidation reactor when a substoichiometric fuel-air mixture or fuel-oxygen partially burns [16,17].

**Copper doped metal oxychloride for hydrogen production**

Copper doped metal oxychloride, sometimes referred to as copper (I) oxide, is one of the greatest photocatalysts. It reflects the p-type semiconductor is common in nature, has a band gap of around 2.20 eV, has low toxicity, and has a high absorptivity of visible light [1,2]. The effectiveness of copper-doped metal oxychloride is limited by the photo- corrosion and the rapid electron-hole pair recombination. They thermodynamically stable under the ambient circumstances, but photo-corrosion significantly reduces its activity upon photo-excitation.
Typically, photoexcited electrons and holes use to cause photo-corrosion. The overall photo-efficiency is

greatly reduced when photocatalytic hydrogen evolution in copper-doped metal oxychloride takes place due to substantial electron-hole pair recombination. In this regard, reduced graphene oxide (rGO) is a two-dimensional substance that possesses exceptional properties such as high surface area and quick electron mobility. The photocatalytic activity will be enhanced by copper-doped metal oxychloride, which will also inhibit the rapid recombination and stop photo-corrosion. The efficiency of hydrogen synthesis is increased by such a procedure, which leads to a more effective charge carrier separation [2,3].

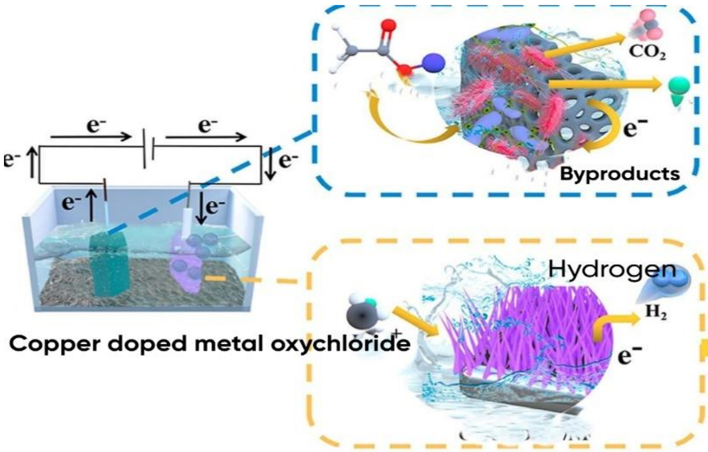


**Fig-3: Shows the scheme of copper doped metal oxychloride for hydrogen production**

Numerous studies have shown that photocatalytic hydrogen production can be improved when precious metals such as Au, Ru, Pt, Pd, and others are added to the surface of copper-doped metal oxychloride. Although using such noble metals might raise the cost of the process, they can also be used in place of less expensive metals with comparable potential to photocatalysts [20,21]. By creating a heterojunction with other composites, copper doped metal oxychloride is able to extend its absorption of visible light and boost its photocatalytic (PC) activity. To improve their efficiency for hydrogen generation, a variety of methods have been developed.

Additionally, by combining copper-doped metal oxychloride with other semiconductor materials, several photocatalysts have been created and studied. It has been proposed that the rate of hydrogen creation can be considerably increased by copper doped metal oxychloride, a metal oxide and a potential photocatalyst with strong photocatalytic activity in hydrogen synthesis. Nevertheless, the photocatalytic activity of copper-doped metal oxychloride is not particularly robust. The quick recombination of the charge carriers that photocatalysts generate limits their utility [22, 23]. It may be used to promote migration and separation in order to address this problem. The photogenerated electrons and holes are used to increase their stability and photocatalytic activity, [23, 24].

Copper-doped metal oxychloride has garnered attention as a photocatalyst for effective solar fuel hydrogen production. Because of its suitable band gap and potential for efficient light absorption in the visible region, copper doped metal oxychloride can generate electron-hole pairs that participate in redox processes and ultimately create hydrogen when exposed to light. Additionally, different factors such as large surface area, an optimum shape, high stability, reusability, and a good bandgap also affected the hydrogen production [24, 25].

**Advantages of producing hydrogen with copper-doped metal oxychloride**

The improvement in hydrogen generation shown by loading of different metal doping nanocomposite materials with copper doped metal oxychloride has resulted in a major revolution.

A method called "metal doping" can increase the material activity by introducing a metal atom, such as an alkali metal reacting with copper metal oxychloride for hydrogen production. The larger wavelength of the doped photocatalyst indicated a photoreaction in the UV light, in contrast to the undoped catalyst. Copper doped metal oxychloride has gained much attention as the other transition metals mentioned for industrial production. Furthermore, the limited amount of available literature on copper doping indicates that the doped catalysts have only been tested in the ultraviolet or near-ultraviolet light spectrum [25,26].

**Role of copper doped metal oxychloride in hydrogen production**

However, it is essential to keep attempting to maximize the copper doped metal oxychloride doping and increase their efficiency [27, 28]. Thin films are made from copper-doped metal oxychloride. The citrate–nitrate method is more effective for hydrogen production using the copper-doped metal oxychloride. These advantages include easy solution processing of the different metal doping, a relatively low heating temperature required for the creation of copper doped metal oxychloride phases, and the ability to adjust layer thickness.

Copper-doped metal oxychloride films showed an outstanding band-edge location with an optical bandgap energy that facilitates high-efficiency water splitting in an integrated tandem system. The electrodes demonstrated the record photocurrent densities for bare films, with a substantial photocurrent start at +0.9 V, as compared to a reversible hydrogen electrode (RHE). It was also discovered that the incident photon-to-current efficiency starts around 830 nm. The exceptional durability of the bare electrodes under operating circumstances for many days set copper doped metal oxychloride apart from previous photocathodes [25,26,28].

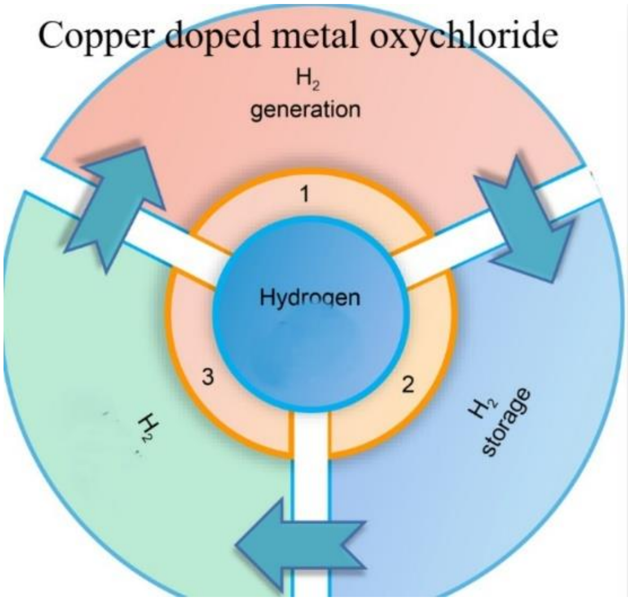


**Fig-4: Shows hydrogen production, via scheme of copper doped metal oxychloride**

Photoelectrochemical hydrogen production has the thermodynamic potential when iron is doped with copper-doped metal oxychloride. Future research will concentrate on altering the deposition circumstances. It is exploring several approaches for creating copper-doped metal oxychloride electrodes doping iron with optimal thicknesses and morphologies. Another component of our research is identifying suitable hydrogen evolution catalysts to include onto the surface of copper-doped metal oxychloride. This strategy seeks to improve the water splitting efficiency of the copper-doped metal oxychloride photocathodes by photoelectrochemical techniques [29, 30].

There has long been research on the application of copper-doped metal oxychloride as a catalyst, particularly in the hydrogen evolution process [19,20].

They exhibits more efficient electrocatalytic activity than one without rotation in a three-electrode setup on a galvanostatic workstation with the electrode rotation. The calculation of several electrochemical parameters gave a detailed understanding of the material's catalytic action [24,27].

Copper doped metal oxychloride, which is the utilized to create the hydrogen through a reaction with chromium, has superior the thermal stability, increased the electrical conductivity. Furthermore, copper-doped metal oxychloride can incorporates anionic organisms, which is advantageous for research on hydrogen energy. The nanoscale delafossite is precipitated from the generated copper-doped metal oxychloride nanopowder. The copper-doped metal oxychloride during the MSR [26,27,28].

Water undergoes a series of intermediate reactions in a thermochemical cycle to separate into hydrogen and oxygen. Typically, it produces a closed cycle with water as the single input and just two products such as hydrogen and oxygen. The copper-doped metal oxychloride uses intermediate copper and chlorine compounds to split water into hydrogen and oxygen [31, 32]. The solid copper-doped metal oxychloride acquires its structure and form in the upstream hydrolysis reactor.

The temperature at which copper-doped metal oxychloride breaks down is higher than its melting point. As a result, molten copper-doped metal oxychloride will be released from the reactor. Molten copper doped metal oxychloride transports high-grade (high temperature) heat, which may be recovered to power other endothermic processes, such as evaporating water to superheated steam for use in the hydrolysis reaction at 375 °C in step 4. HCl gas may also be heated from 375 °C to 450 °C for use in the hydrogen production process [33, 34].

On an industrial scale, the steam may be reused in other processes, such as the hydrolysis stage. A liquid that travels through the heat would be created in the auxiliary equipment by cooling vapor that travels through the pipe of a vertical heat exchanger. To prevent any dangerous gas escapes into the environment, the condenser should offer rapid cooling [35, 36]. Copper-doped metal oxychloride is a potential thermochemical for nuclear-powered hydrogen production. It shown that the copper-doped metal oxychloride might have a thermal efficiency of up to 53% when losses from the operation of engineering equipment are taken into consideration, however 43% is more realistic. The scientific feasibility of all thermal processes has been demonstrated, and they all proceed to completion with very few side reactions [31, 34].

Many techniques for efficiently the dissecting water into its component parts are demonstrated by the production of hydrogen using copper-doped metal oxychloride. At the beginning of the process, hydrogen gas and molten cuprous chloride are created when copper and HCl gas mix. Next comes the disproportionation of cuprous chloride into aqueous cupric chloride and copper. This cycle maintains a pressure of 1 bar while operating between 450 and 530 °C. There are four steps in the copper doped metal oxychloride cycle. First, hydrogen and aqueous cupric chloride are produced by the reaction of aqueous cuprous chloride and hydrogen chloride. The aqueous cupric chloride is then solidified during the drying phase. Copper-oxychloride and hydrogen chloride gas are produced when solid cupric chloride undergoes hydrolysis, a reaction with water [34, 35].

Copper-oxychloride breaks decomposed thermally to produce oxygen gas and cuprous chloride. The five-step copper doped metal oxychloride cycle begins at 400 °C when cupric chloride and water hydrolyze to create copper-oxychloride and HCl gas. The breakdown of copper-oxychloride results in the production of molten cupric chloride and oxygen. In a copper generation process, cuprous chloride is converted back into cupric chloride and copper. The cycle is completed when cupric chloride is isolated from water after the copper and HCl gas mix to generate hydrogen at 430 °C. The method of producing hydrogen by electrolyzing copper-doped metal oxychloride under different conditions [36, 37].

An electrochemical method for the hydrogen creation has several advantages over conventional water electrolysis. It produced hydrogen in a number of copper-doped metal oxychloride procedures. Nafion-based membranes are used with an anolyte of 1-2 mol/L (M) CuCl in a 6 M HCl solution, where the 6 M HCl solution acts as a catholyte. The electrolysis step uses a copper-doped metal oxychloride catalyst membrane electrode. Between 91% and 99% hydrogen production was observed, and there was no copper deposition on the electrolyser's constituent

parts. Temperature is the main factor in enhancing performance, whereas anolyte and catholyte flow rates were shown to have no appreciable effect on performance [38, 39].
The copper crossing from anode to cathode was seen for several tested membranes. Copper precipitation and this crossover must be avoided by an efficient electrolyser. The stack efficiency rose from 68% to 72% as the temperature rose from 298 to 333 K. Higher efficiency was observed at the cell near the analyte and catholyte input ports than at other cells because less electrolyte was received in the middle of the stack. A fully built electrolysis cell capable of producing 50 L/h of hydrogen at 353 K with a cell concentration of 2 mol copper doped metal oxychloride and 0.4 A/cm2 was disclosed by Canadian Nuclear Laboratories (CNL) [39, 40].
Reducing the water required for the hydrolysis process is the most difficult step in the hydrolysis of copper-doped metal oxychloride, as it may cause cupric chloride to break down [31, 32]. A vertical fluidized bed arrangement requires more steam for fluidization and raises the energy needs of the cycle. Several methods have been employed in the past to dehydrate copper doped metal oxychloride solutions [33, 34].
For copper-doped metal oxychloride, the use of internal heat to lower heat load via a network of heat exchangers was previously studied. The thermal management and conducted simulated experiments using the Aspen energy analyser. The heat needed for hydrolysis and drying processes can be satisfied by the recovered heat. Exergy destruction was used to analyse each arrangement. In contrast, these values were 334.4, 782.1, 491.8, and 363.7 kW, respectively, for the baseline scenario [35, 36].
One of the main issues facing the future hydrogen economy is finding a more cost-effective and ecological method of creating hydrogen with reduced need on fossil fuels. Thermochemical water splitting, which uses intermediate copper and chlorine compounds, is a workable alternative that can be linked to nuclear reactors to thermally split water into hydrogen and oxygen. Heat is either transported across processes or recovered from specific processes [20, 31]. It also examines the thermal design of the oxygen production reactor, which is an important stage in the process of splitting water by dissolving an intermediate chemical. The equipment design is analyzed to scale up earlier work in small proof-of-principle test tubes to a larger capacity of oxygen production using engineering lab-size equipment [33, 34].

**Challenges in hydrogen production**

In addition to being created from renewable energy sources, hydrogen may be produced from fossil fuels using a variety of processes, such as gasification, steam reforming, partial oxidation, and auto thermal oxidation. Hydrogen may be produced by gratifying biomass or biofuels and splitting water using solar or wind energy [35, 36]. Every year, coal is used to extract around 21.5 billion tons of hydrogen, which needs to be replaced by renewable energy sources. The production of ammonium and the upgrading and desulfurization of conventional petroleum will result in a significant need for H2 [36,37]. Greater H2 generation with existing technology will increase greenhouse gas emissions and necessitate the use of more conventional fuels [38, 39, 40].

**Conclusion and future perspectives**

Recent research has focused a lot of attention on copper-doped metal oxychloride due to its emerging properties. The charge carrier profile and high electron mobility of copper-doped metal oxychloride result in a relatively low level of thermal stability. Numerous industries, including wastewater treatment, supercapacitors, microwaves, and many more, have used copper doped metal oxychloride and its composites. Through water splitting, they offer substantial advantages in photocatalytic hydrogen generation.
Numerous obstacles for hydrogen generation using metal oxides, mostly attributable to inefficiency and material constraints. Elevated temperatures necessary for some cycles, optimal efficiency of photocatalytic water-splitting, and costly noble metal catalysts are needed to improve for high production. Moreover, safety issues related to hydrogen production and need for enhanced infrastructure for storage and transportation still facing challenging. Advancements in materials science and nanotechnology present the promising opportunities for future development, such as employing heterostructures and novel metal compounds to improve photocatalytic water splitting,

as well as creating efficient and stable metal oxide catalysts for hydrogen evolution reactions.

The non-noble-metal photocatalysts provide potential options for water splitting due to their high efficiency. Furthermore, non-noble metal photocatalysts have high stability to Pt deactivation in the presence of halide ions. This renders the non-noble metal photocatalysts appropriate for the transformation of wastewater into the hydrogen production. Nonetheless, despite the advantages, there is a scarcity of evaluations about the photocatalytic production of hydrogen with non-noble metal photocatalysts. The technique for comprehensively investigating the enhancement of hydrogen production efficiency in non-noble metal photocatalysts requires more exploration at industrial scale to improve the production status.

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