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# Metal Organic Frameworks (MOFs) for Sustainable Hydrogen Fuel Production

Over the last few decades, scientists worldwide have sought for viable and cost-efficient catalysts for photocatalytic water splitting (Song et al, 2017). Currently, metal oxides such as $TiO_2$ and NiO help convert solar energy into a more accessible chemical form; however, their low surface area and limited morphology prevent industrial-scale application (Ipek & Uner, 2019). By implementing metal-organic frameworks (MOFs), desirable features like high surface area, rich composition and structural versatility may be accessed to efficiently produce hydrogen fuel (Wang et al, 2017). This scientific advancement demonstrates the SHE concept *Applications and Limitations*, as enhanced understanding and integration of renewable hydrogen production can mitigate air pollution and improve civilians' quality of life, highlighting the interaction between science and society. However, their inability to photo-catalyse under visible light and potential instability in water present challenges which need to be addressed, so that MOF-based catalysts may achieve desired the functionality and widespread integration into society.



Photocatalytic water splitting is a form of artificial photosynthesis whereby catalysts accelerate the electrolysis of water (Wang et al, 2017). These photo-catalysts provide an alternative pathway by lowering the activation energy required to initiate the reaction, thus speeding up the conversion of sunlight and water into hydrogen and oxygen, shown in Figure 1 (Clark, 2018). In a photo-electrochemical cell, MOFs are situated at the anode to accelerate the water oxidation process, resulting in electron flow towards the cathode to reduce protons into hydrogen fuel (Figure 2). The water-splitting reaction can be expressed by the following redox half-equations:

1. Oxidation/dissociation of water into oxygen, protons and electrons
   $2H_2O_{(l)} + \text{energy} \rightarrow O_{2\,(g)} + 4H^+_{(aq)} + 4e^-$
2. Reduction of protons to produce dihydrogen fuel
   $4H^+_{(aq)} + 4e^- \rightarrow 2H_{2\,(g)}$

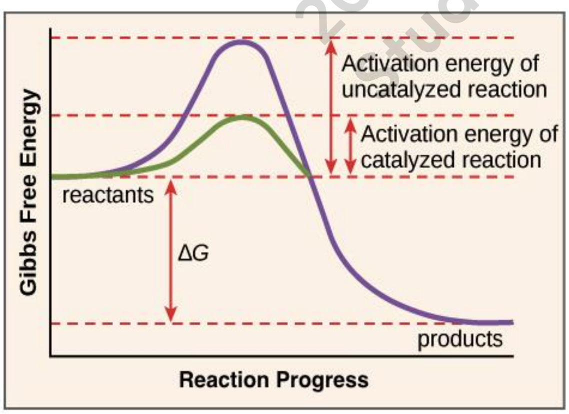


Figure 1. Energy profile depicting lower activation energy as a result of catalyst presence. Image retrieved from Avissar (2013).

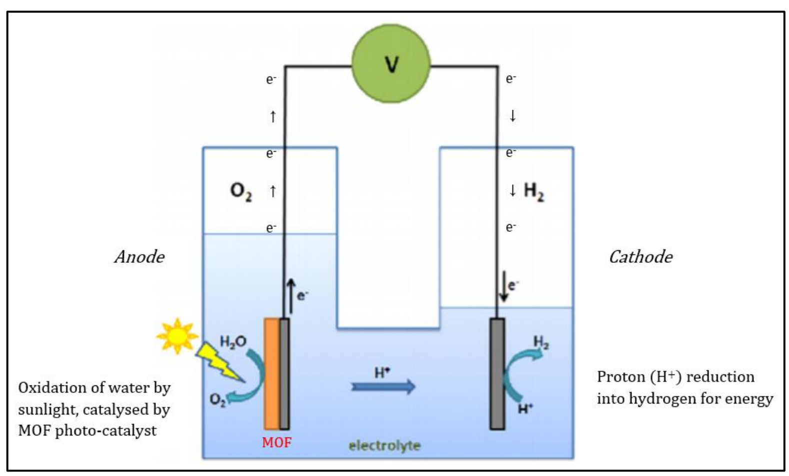


Figure 2. Photo-electrochemical cell with MOF (at anode) to catalyse the electrolysis of water into hydrogen (at cathode). Image retrieved from Ahmad et al (2014).

Recently, MOF-based photo-catalysts have received emerging recognition for their unprecedented morphology and versatile properties (Wang et al, 2012). MOFs are primarily composed of organic bridging ligands containing functional groups, which are connected to metal cation clusters by coordination bonds and weak intermolecular forces to form a three-dimensional, crystalline network (Alshammari, 2016). An example can be seen in Figure 3, depicting a MOF photo-catalyst composed of zinc clusters and 1,4-benzenedicarboxylic acid subunits which has shown potential in gas separation. The rigid benzene ring structure of MOFs generates the microscopic porosity central to their function, and amplifies the thermal and mechanical stability throughout the framework (Lin et al, 2014). These pores, coupled with open, unsaturated metal sites and catalytically-active organic ligands, promote superior catalytic performance due to their low density, facilitation of solvent exchange, intrinsically high surface area, and tunable structure, enhancing interaction between substrates and reaction sites (Song et al, 2017).

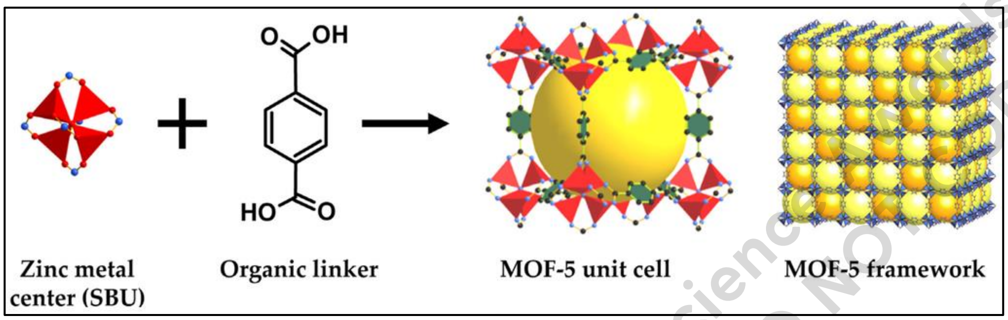


Figure 3. Example of zinc ionic cluster and organic linker used in MOF synthesis.
Image retrieved from Perez et al (2016).



Through interdisciplinary research, collaboration and careful monitoring of this technology, scientists have discovered that when light energy equivalent to the bandgap (usually 1.23V) is absorbed, photoexcitation migrates electrons to the conduction band and a positively-charged carrier is propagated on the MOF photo-catalyst surface (Ipek & Uner, 2019). The aforementioned physical and chemical properties heighten the ability of electrons and carriers on MOF surfaces to absorb water substrates, thereby increasing the rate of reaction for clean and viable hydrogen production (Qiu et al, 2018).

One of the predominant social benefits of MOF-based photocatalytic water splitting is its derivation from sunlight and water, raw materials which are available in almost unlimited amounts (Barber & Tran, 2013). In recent decades, significant human population growth and industrialisation has led to burgeoning global energy demands. By using MOFs to effectively convert readily-available resources into large quantities of hydrogen fuel, humans can become independent of fossil fuels whilst also meeting energy demands for the powering of local infrastructures and technologies (Royal Society of Chemistry, 2012). Moreover, application of this research and technology will enhance living conditions for humans and organisms on Earth. Prolonged and amplified exposure to air pollution and photochemical smog from fossil fuel combustion provokes detrimental health consequences such as elevated risk of cardiovascular disease, respiratory illnesses, and certain cancers (World Health Organisation, 2020). MOF-mediated solar hydrogen production therefore decrease pollutant emissions to alleviate global air quality and improve civilians' quality of life, particularly individuals suffering from respiratory diseases like asthma, and developing nations like India, Pakistan and Bangladesh where the current economy impedes integration of sustainable energy alternatives (NSW Government, 2013).

Photocatalytic water splitting using MOFs can also make poignant contributions to economic growth. Many common products, such as pharmaceuticals, plastics and fertilisers, utilise fossil-fuel-based hydrogen feedstock, which require substantial proportions of energy to synthesise (Royal Society of Chemistry, 2012). The capability of MOFs to produce hydrogen feedstock from readily-available natural resources like sunlight and water will improve production and yield in industries such as chemical engineering, manufacturing and agriculture, helping increase exports to raise the financial gains and Gross Domestic Product of entire nations (Agarwal, 2020). While moving on from fossil fuels may result in potential unexpected ramifications such as loss of jobs in the mining industry, the requirement for more labor throughout the multi-faceted water splitting process will introduce new employment opportunities, creating more income and demand for goods which will benefit the global economy (DCED, 2020). MOFs' durability is another economic asset, as their lifetime transcends the energy and resources required to install them, thus making their application commercially viable and highly cost-effective (Royal Society of Chemistry, 2012).

Though cheap and easily-processed into hydrogen, fossil fuels are finite and proliferate the greenhouse effect, causing extreme weather patterns, natural disasters, photochemical smog, melting of sea ice and ocean acidification to become alarmingly frequent and severe (Environmental Defense Fund, 2020). These disastrous ramifications harm not only humans, but also flora and fauna species inhabiting these ecosystems, potentially disrupting global food webs and greatly diminishing the biodiversity essential for ecological survival (Earth Institute, 2018). While affluent, renewable energy sources such as solar panels, windmills and hydropower are currently being integrated, their heavy-reliance on environmental conditions and inefficient transportability make them inconvenient for practical use (Radhakrishnan et al, 2017). MOF-mediated photocatalytic water splitting thus rectifies this issue by storing the solar radiation into the chemical bonds of the fuels, enabling efficient energy supply without compromising the Earth's natural environment (Royal Society of Chemistry, 2012). Reducing the emission of harmful waste products such as $CO_2$, $CH_4$, $N_2O$ and ozone ($O_3$) which absorb re-radiated solar radiation and contribute to the enhanced greenhouse effect will be accompanied with profuse benefits such as lower risk of damage to infrastructures, lessened soil degradation, and more secure global aquatic environments (DAWE, 2020). Through this, vulnerable ecosystems may be protected to ensure biodiversity and maintain the natural ecological balance (Environmental Defense Fund, 2020).

Although the application of MOF-based photo-catalysts can introduce profuse beneficial impacts, a current limitation is their inability to convert visible light into energy. Numerous attempts have been made by scientists and researchers to develop advanced models that work efficiently not only under UV radiation, but also under the visible light spectrum; however, unavailability of materials that can surpass its large bandgap hinder present resolutions (Zhang & Lin, 2012). As 46-50% of solar energy is dispersed as visible light, further testing of novel material combinations for MOF synthesis must be pursued to overcome the restrictions of insufficient data (NASA, 2003). Conquering this challenge will allow greater percentage conversion efficiency of solar hydrogen to be achieved.

Another major concern is the poor stability of MOF-based catalysts in water, which is attributed to unanticipated higher ionic affinity of the metal ions to water molecules than organic ligands (Wang et al, 2017). As water is a precious commodity required for numerous daily activities, potential leaching of metallic and organic components from MOFs during the photocatalytic reaction is a paramount problem demanding immediate rectification (Tan et al, 2015). Along with contamination of valuable water supplies, this consequence may cause severe detriment to marine life and habitats nearby MOF sites (Ipek & Uner, 2019). Therefore, further investigation into the mechanisms and structure of photo-catalysts are required to eliminate these risks and ensure safe, long-term integration of the technology into society. However, to prevent inaccurate answers and unanticipated negative outcomes, careful risk assessment and peer-review from multiple fields alongside chemistry must be attained during consolidation of limitations, such as the collaboration of engineering and other sciences throughout the MOF development process.

It is anticipated that the global demand for energy will soar rapidly within the next few decades. Fulfillment of society's energy needs will require concerted inputs from scientists and researchers to harness the untapped potential of solar radiation, thus enabling economic growth and alleviation of the catastrophic prospects of climate change. Recent progress in photo-catalytic MOFs have illuminated their promising potential for sustainable hydrogen fuel production. However, surpassing the present limitations of industrial-scale viability are significant challenges which must not be overlooked.

**Word Count: 1410 words**

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