



Molecular Catalysis in “Green” Hydrogen Production

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Molecular hydrogen (H₂) is considered an ideal energy vector and a clean fuel, due to its zero-carbon combustion. Nevertheless, despite hydrogen is the most and one of the most abundant elements in the universe and in earth crust, respectively, it is always combined with other elements in our planet and never appears in its elemental state. This means that H₂ must be produced through, almost always, endergonic processes, whose sustainability depend not only on the starting material but also on the source of energy necessary for these processes to occur. Colors have been assigned to identify the level of sustainability of H₂ production with the green one indicating H₂ produced from water using a renewable source of energy, preferably sunlight. Redox water splitting (WS) into H₂ (hydrogen evolution reaction, HER) and O₂ (oxygen evolution reaction, OER) is, nevertheless, an extremely difficult process not only from the thermodynamic but also from the kinetic point of view. Relevant kinetic barriers are present in both sides of the redox process, especially in OER. For this reason, performing WS in an efficient manner requires the development of active and robust catalysts capable of offering alternative reaction pathways to WS, lowering down the unfavorable kinetic barriers and thus maximizing the energy conversion efficiency. Inspiration for developing efficient catalysts for HER and OER has traditionally derived from Nature, who, over the course of many billions of years, according to the evolutionary theory, has assembled two molecular catalytic pools, namely oxygen evolving complex and ferredoxin/ferredoxin NADP⁺ reductase, which offer viable kinetic pathways to both OER and reduction of NADP⁺ (the “biological form” of H₂). In reality, after several attempts of mimicking natural catalysts, the efforts of the researchers have been addressed to different molecular systems, which exhibit best performances, unfortunately often based on noble-metal atoms, especially for OER. In this contribution we review the journey of the development of molecular catalysts for both HER and the OER, highlighting selected systems, which have brought us to the current level of knowledge.

Keywords: green hydrogen, water oxidation, hydrogen evolution, homogeneous catalysis, organometallics

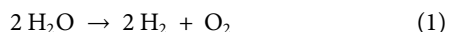
Abbreviations: WS, water splitting; OER, oxygen evolving reaction; HER, hydrogen evolving reaction; WO, water oxidation; WOC, water oxidation catalysts; TON, turnover number; TOF, turnover frequency; Cp*, pentamethylcyclopentadienyl; NADPH, nicotinamide adenine dinucleotide phosphate; PEC, photoelectrochemical cell; PVE, photovoltaic-coupled electrolyzer; DMF, dimethylformamide; PCET, proton-coupled electron transfer; SO, sacrificial oxidant; CAN, cerium ammonium nitrate; bda, 2,2'-bipyridine-6,6'-dicarboxylate; pycal, 2-(2'pyridyl)-2-propanolate.

INTRODUCTION

The current climate and energy crises urgently require the identification of a sustainable alternative to fossil-derived fuels. Molecular hydrogen is emerging as the leading candidate to fulfil this role, owing to its non-toxicity, high energy per unit mass (120 MJ kg^{-1}) and zero combustion emissions (European Commission, 2020; IEA, 2020; Crabtree et al., 2004; Parra et al., 2019; Griffiths et al., 2021). The sustainable supply of H_2 on a global scale, however, poses some serious technological challenges (Song et al., 2022). Both production and storage of H_2 are, indeed, non-trivial. Even though it is one of the most abundant elements on Earth, hydrogen is not directly available as it is bound to other elements in natural organic and inorganic molecules, some of them being the feedstocks for a variety of industrial H_2 production processes. To establish sustainability metrics for the latter processes, the scientific community has felt the need to attribute *colors* to hydrogen, which is, notoriously a colorless molecule (**Figure 1**) (Newborough and Cooley, 2020; Griffiths et al., 2021).

At present, the vast majority of commercial hydrogen is produced *via* steam reforming or partial oxidation of non-renewable fossil feedstocks, like coal (*black hydrogen*), natural gas (*grey hydrogen*) and lignite (*brown hydrogen*) (Griffiths et al., 2021). In a short-term perspective, many efforts are devoted to limit the carbon footprint of these production processes. Some examples include integrating them with carbon capture and utilization systems (CCSU; *blue hydrogen*), or opting for methane pyrolysis, which produces solid carbon residues as byproduct rather than gaseous CO_2 (*turquoise hydrogen*) (Newborough and Cooley, 2020). Nevertheless, the transition from fossil to renewable raw materials is essential for long-term sustainable hydrogen production.

Water splitting (WS) appears to be the ideal approach in this respect, being based on a cheap, non-toxic and renewable starting material like H_2O , and providing O_2 as the only benign byproduct (Armaroli and Balzani, 2007):



The main limit of this approach lies in its unfavorable kinetics and thermodynamics. Using fossil-derived electricity to drive such energy demanding process is clearly unreasonable. Although relatively small amounts of "low-carbon hydrogen" are currently produced by water electrolysis using nuclear power (*purple hydrogen*) or grid electricity (*yellow hydrogen*) (Griffiths

et al., 2021), the production of truly *green hydrogen* is necessarily bound to the combination of renewable feedstocks, like water, and energy sources, ideally sunlight (Lewis and Nocera, 2006; Armaroli and Balzani, 2007; Velazquez Abad and Dodds, 2020). This latter process would mimic natural photosynthesis, exploiting sunlight to drive the water oxidation (WO) half-reaction, and then using the resulting protons and electrons to reduce NADP^+ to NADPH cofactor and, consequently, CO_2 to carbohydrates (Kärkäs et al., 2014). In both cases, light is the primary energy source, while chemical bonds -of either H_2 or NADPH- serve as a kind of accumulator to deliver the energy packages where needed.

To realize an artificial photosynthesis device two aspects are critical: 1) developing efficient systems for harvesting solar energy, and 2) optimizing its conversion into chemical energy in the form of H-H bonds. Two main types of devices are typically utilized: photovoltaic-coupled electrolyzers (PVE, **Figure 2**) and photoelectrochemical cells (PEC, **Figure 2**). In PVEs, a photovoltaic cell provides the necessary overpotential to drive WS in the electrolyzer; in PECs, sunlight is instead harvested by a photoanode having suitable valence band potentials to carry out the oxidative half-reaction, with the generated electrons being transferred to the photocathode for proton reduction (Ager et al., 2015). In both approaches, one of the main hurdles towards the development of efficient WS devices lies in the high overpotentials needed, especially for the WO half-reaction. The identification of highly active and robust catalysts is therefore essential for knocking down such unfavorable kinetic barriers.

Over the last few decades, research in catalyst discovery and optimization has sparked, providing a plethora of catalytic systems for both half-reactions. Despite significant progress has been made, the identification of high-performing catalysts for large scale applications remains an open challenge.

Along with heterogeneous systems, molecular catalysts based on coordination compounds have drawn significant attention (Esswein and Nocera, 2007; Wang et al., 2009; Wang et al., 2012 M.; Eckenhoff and Eisenberg, 2012; Berardi et al., 2014; Zhang and Sun, 2019a; Barrozo and Orio, 2019). Their well-defined molecular nature offer some advantages, primarily in terms of atom efficiency, as molecular catalysts typically guarantee nearly 100% active metal centers; this is especially important when noble metals are employed (Zhang and Sun, 2019a; Macchioni, 2019). Furthermore, their reactivity can be tuned by structural

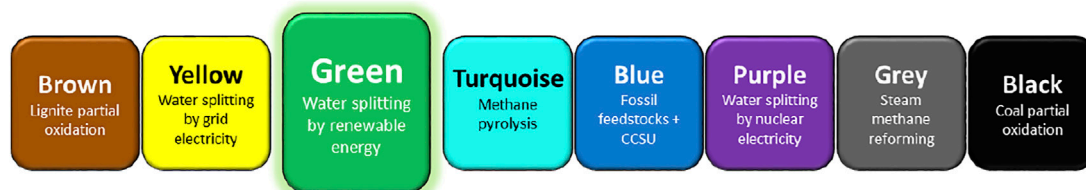
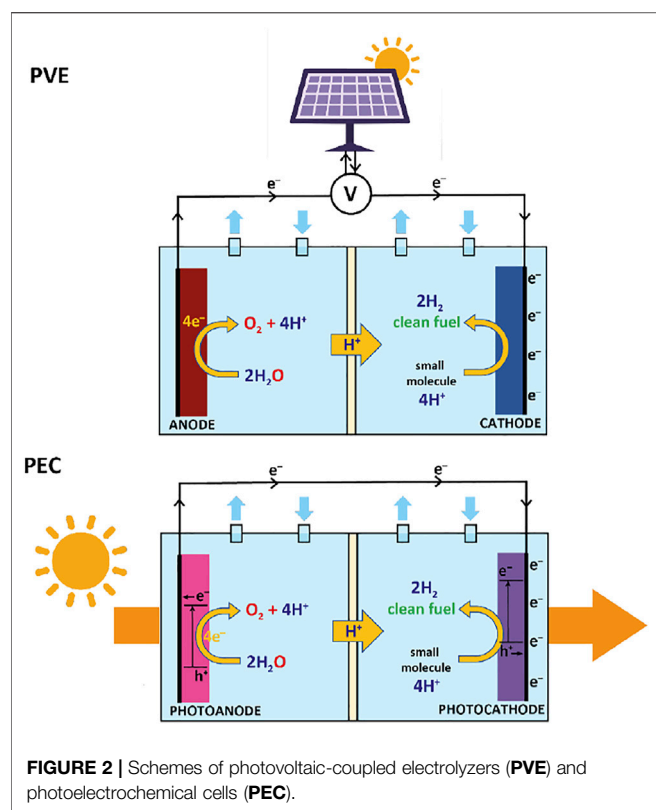


FIGURE 1 | The colors of hydrogen production processes.



tailoring to enhance activity. In this respect, it is also important to note that, with respect to heterogeneous systems, the activity of molecular catalysts can be more easily described in terms of performance parameters like turnover number (TON) and turnover frequency (TOF), facilitating kinetic and benchmarking studies that are essential for rational catalyst development (Kondo et al., 2021). These are the reasons why many efforts are devoted towards the development of water splitting devices involving molecular catalysts, having in durability and recyclability their Achilles' heel.

This Review highlights the role which molecular catalysts might have in the pursuing of sustainable global energy supply. The discussion will focus on both half-reactions of water splitting, namely the hydrogen (HER) and oxygen (OER) evolution reaction, summarizing selected milestones, persisting bottlenecks, and foreseeable prospects.

HYDROGEN EVOLVING REACTION CATALYSTS

In nature, reversible H_2 oxidation is catalyzed by [FeFe], [FeNi] or Fe hydrogenase enzymes (Zhang and Sun, 2019a) in combination with cofactors/coenzymes that contribute synergistically to reaction thermodynamics.



As outlined before, proton reduction is realized in the laboratory either electrochemically (Wang M. et al., 2012) or photochemically (Sakai and Ozawa, 2007; Stoll et al., 2015; Eckenhoff, 2018; Amaro-Gahete et al., 2021). With a few exceptions, most classes of catalysts are active in both processes. Herein we will focus on electrocatalysis, aiming at sketching out the main branches of research in homogeneous HER and setting future directions in catalyst design.

The obvious starting point has been to take inspiration from natural enzymes. Rauchfuss and coworkers demonstrated in 2001 the suitability of the structural hydrogenase model **1** (Figure 3) in electrocatalytic H_2 generation (Gloaguen et al., 2001). Since then, the field has become very active (Capon et al., 2005, 2009), but hydrogenase models revealed to suffer from poor solubility in water and scarce resistance towards strong acids. Therefore, most studies are performed in organic media, which are not an ideal choice when designing a sustainable device for WS. Hydrophilic substitution (Na et al., 2006) or encapsulation in cyclodextrins (Singleton et al., 2010) can all be used to solubilize hydrogenase models in water, but applications are still very limited. [NiFe] models such as **2** also show moderate activity at 400–430 mV overpotential, with rate constants in the order of 50 s^{-1} in CH_2Cl_2 (Barton and Rauchfuss, 2010). Mn dimers **3** and **4**, with structural features resembling hydrogenase cores, showed higher activities than [FeFe] and [FeNi] models. These species can reduce protons at moderate overpotentials (550–650 mV) in either DMF or MeCN, with TOF up to 44600 s^{-1} (Hou et al., 2014; Hou and Fan, 2014).

Overall, such catalytic performance is still not satisfactory enough to foresee applications of hydrogenase models in H_2 generation technologies in the next future. In stark contrast, mononuclear complexes of earth-abundant metals offer a solid alternative, with some species showing activities comparable (or even higher) than that of natural enzymes (TOF or k_{cat} in the order of $1\text{--}2 \times 10^4 \text{ s}^{-1}$) (Frey, 2002). It must be noted that a direct comparison between different systems is difficult, owing to the very different experimental conditions used in electrocatalysis. Particular attention must be paid to overpotentials, as highly active systems tend to work at high overpotentials. The ideal catalyst should show high activity at low overpotential and only very few electrocatalysts are able to do so, as yet.

Striving for the ideal HER electrocatalyst, a few families of compounds stood out during the past two decades. A first notable example is the class of polypyridyl (Zee et al., 2015) and pyridyl-amine complexes of Mo, Co. (Sun et al., 2011), Ni (Zhang et al., 2014c) and Cu. Long, Chang and co-workers reported that the Mo(II) species **5** activates water catalytically and, under controlled electrolysis conditions at pH = 7, produces H_2 with TOF approaching 2.4 s^{-1} and TON values of 6.1×10^5 at an overpotential of 640 mV (Karunadasa et al., 2010). Complex **6**, a soluble mimic of molybdenite (Karunadasa et al., 2012), a very efficient heterogeneous HER catalyst (Jaramillo et al., 2007), also catalyzes electrochemical proton reduction in both MeCN and water, with optimal activity observed at pH = 3. A TOF up to 280 s^{-1} was observed at 828 mV overpotential. Interestingly, both **5** and **6** showed catalytic activity for H_2 production when tested with seawater. The Cu complex **7** is another remarkably active

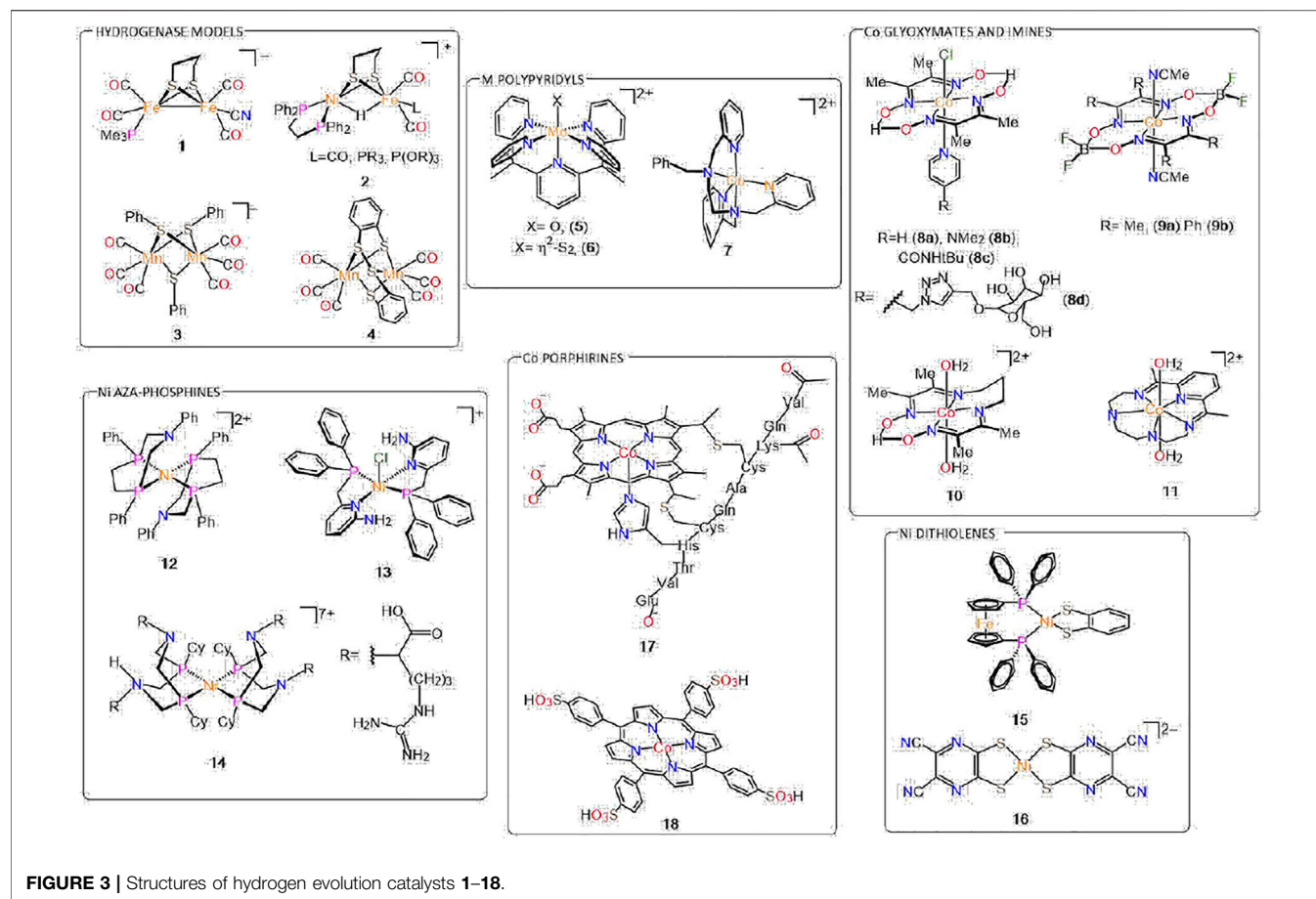


FIGURE 3 | Structures of hydrogen evolution catalysts 1–18.

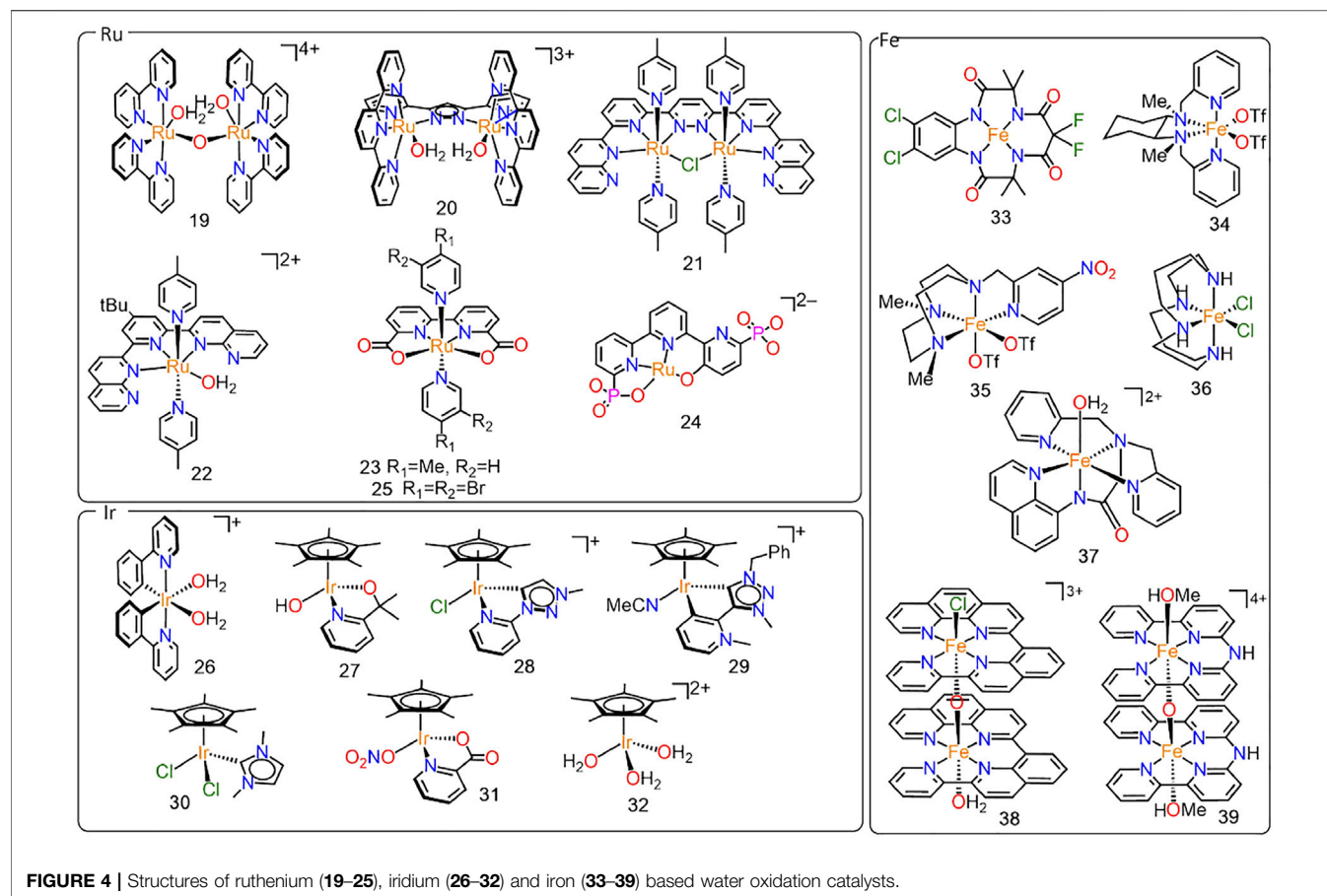
catalyst, evolving H_2 with a k_{obs} of over 10000 s^{-1} at $\text{pH} = 2.5$ and 420 mV overpotential. Mechanistically, the reaction is supposed to occur upon two consecutive PCET events, affording a Cu(II) hydride intermediate with a protonated ligand, which undergoes H_2 elimination and regenerates the catalyst (Zhang et al., 2014b).

Cobalt glyoximate complexes are also excellent catalysts for H_2 electroproduction, offering cheaper alternatives to Pt and showing high activities at reduced overpotentials (Artero et al., 2011). Co(III) complexes **8**, which are active in proton reduction in DMF/[HNEt₃][Cl] and, particularly at low acid loading, show higher activities when more electron-donating groups are introduced (TON of 100 over 2.5 h, when $\text{R} = \text{H}$, **8a**). To improve water solubility, Zhang and co-workers functionalized the pyridine ring with a triazole-glucose pendant group and obtained complex **8d**, an electrocatalyst able to work under neutral conditions at an overpotential of 341 mV (Yin et al., 2015). Co(II) glyoximates **9** are comparatively more active and reduce protons from a broad set of acids with modest to low pK_a in MeCN at very low overpotentials. For example, HOAc^{F} is reduced at less than 50 mV overpotential with an estimated k_{obs} of 770 s^{-1} (Hu et al., 2005).

To overcome the instability of cobaloximes towards hydrolysis, imine/oxime catalysts have been developed. This class of catalysts is a notable step forward, as they retain catalytic activity in neat water. Complex **10** catalyzes proton

reduction in water at $\text{pH} = 2.2$ with a rather low overpotential of 390 mV , affording 23 turnovers (McCroary et al., 2012). More recently, Zong, Lu and Sakai reported the Co macrocyclic complex **11**, which represents a kind of evolution of the imine glyoximate scaffold (Wang et al., 2019). **11** is an extremely efficient electrocatalyst and can reduce protons at $\text{pH} = 7$ with a k_{cat} of 2210 s^{-1} at 680 mV overpotential. On top of its good catalytic performance, **11** is tolerant to O_2 and CO , making a good candidate for application in H_2 generation devices and fuel cells.

The combination of multidentate azophosphine ligands and first row transition metals originates an outstanding class of electrocatalysts for H_2 oxidation and production (Dubois and Dubois, 2009). Following up on previous work (Wilson et al., 2006), Bullock, DuBois and coworkers reported in 2011 that the dicationic Ni(II) complex **12** is a robust and highly efficient catalyst for proton reduction in MeCN, using [(DMF)H]OTf ($\text{pK}_a = 6.1$) as proton source (Helm et al., 2011). Catalytic activity was observed at an overpotential of 625 mV and a remarkable TOF of 106000 s^{-1} was obtained in the presence of traces of H_2O . The ability of the pendant-N group to act as a positioned proton relay is proposed to be the key mechanistic concept, mimicking somehow what is proposed to occur in natural [FeFe] hydrogenases (Léger and Bertrand, 2008). A similar concept was later explored by Masuda with the Ni(II)



phosphinopyridyl complex **13**, containing amino groups able to act as proton relay. **13** catalyzes HER in MeCN/[NBu₄][ClO₄] using acetic acid as proton source, with TOF values up to 8400 s⁻¹ at an overpotential of 590 mV (Tatematsu et al., 2016). To enhance water solubility of this class of compounds, DuBois and co-workers functionalized the -N groups of the [Ni(P₂N₂^R)₂]²⁺ motif with biomimetic aminoacidic fragments, such as glycine and arginine (Dutta et al., 2014). These functionalized complexes showed reversible catalytic activity, even at elevated temperatures, and could be used for both H₂ oxidation and production. The arginine derivative **14** revealed to resist a broad set of pH conditions, ranging from 0.0 to 6.0, and showed high TOF values at 348K, comparable to those of [NiFe] hydrogenases. **14** tolerates exposure to CO, therefore showing great potential for working in fuel cells.

Another branch of HER electrocatalysts is constituted by homoleptic metal-dithiolenes, which emerged after the first reports by Holland/Eisenberg (McNamara et al., 2011) and Sarkar (Begum et al., 2010). In 2015, Jones and coworkers showed that also the heteroleptic diphosphine-dithiolene complex **15** catalyzes HER in THF, with TOF up to 1240 s⁻¹ and overpotentials as low as 265 mV (Gan et al., 2015). Even though catalytic performance of **15** is promising, its poor solubility in water hampers any real-life application. In 2017, Yamauchi, Sakai and coworkers reported the anionic Ni complex

16, which is water soluble and catalyzes HER at relatively low overpotentials (330–400 mV at pH 4–6). Bulk electrolysis experiments reached a turnover number of 20000 over 24 h, indicating that this family of catalysts is highly durable (Koshiba et al., 2017). Mechanistically, a series of consecutive, ligand-based, PCET events is proposed to be the origin of the reduced overpotentials (Aimoto et al., 2018).

A last branch involves metal porphyrins, which have long been known to be active electrocatalysts for H₂ production but did not attract much interest owing to poor activity and high overpotentials (Kellett and Spiro, 2002). However, proper tuning of functional group can increase the catalytic performance of these species and, at the same time, impart a high solubility in water. For example, the group of Bren reported in 2014 that acetylated cobalt mycoperoxidase-11 (**17**) is an active bioorganometallic catalyst for proton reduction. In aqueous solution at pH 7.0, **17** showed promising initial TOF (6.7 s⁻¹ after 10 min) and TON values (2.4 × 10⁴), at an overpotential of 852 mV. Such an enhancement of activity was ascribed to the presence of the axial imidazole group from the peptide unit. Interestingly, **17** tolerates exposure to oxygen and retains catalytic activity in air, which is an important feature for the ideal catalyst for hydrogen evolution. However, the activity of **17** decreases over time owing to degradation under electrolytic conditions (Kleingardner et al., 2014). To enhance catalyst's

durability, Hung and coworkers used the *p*-sulfonatophenyl complex **18** for electrocatalytic proton reduction in neutral water, obtaining good performance both in terms of TOF (up to 1.8 s^{-1}) and TON (1.9×10^4) over a 73 h reaction time at 876 mV overpotential (Beyene et al., 2015).

OXYGEN EVOLUTION REACTION CATALYSTS

OER is the half-reaction of WS providing the electrons and protons necessary for hydrogen liberation. It requires a complex series of multielectron/multiproton transfers and represents the thermodynamic and kinetic bottleneck of the overall process:



To guarantee good activity and durability, efficient water oxidation catalysts (WOCs) must be able to easily accumulate multiple charges at the metal center without triggering degradation processes. The nature of the metal center is therefore crucial and evolution of ancillary ligands for WOCs has followed rather specific routes for each catalytically active transition element (vide infra).

The possibility of using sacrificial oxidants (SO), like cerium ammonium nitrate (CAN) and NaIO_4 , to drive OER has largely facilitated the screening of molecular WOCs, to the point that relatively few electrochemical studies have been reported. It should be noted here that comparing catalytic activities is a delicate task, since it strongly depends on experimental conditions, like the nature of the sacrificial oxidant (e.g., CAN vs. NaIO_4) (Codolà et al., 2015; Pokhrel et al., 2015; Bucci et al., 2016; Mazloomi et al., 2020) or the electrochemical method used (Diaz-Morales et al., 2014; Kottrup et al., 2018; Olivares et al., 2020; Van Dijk et al., 2020).

Noble metals like ruthenium and iridium have shown the overall most promising performances (Blakemore et al., 2015; Matheu et al., 2019), and this is why many groups are trying to develop WOCs with a "noble metal atom economy" approach to minimize the use of such precious elements (Ledendecker et al., 2019; Macchioni, 2019). Starting from the Meyer's "blue dimer" *cis*- $[(\text{H}_2\text{O})\text{Ru}^{\text{III}}(\text{bpy})_2(\mu\text{-O})\text{Ru}^{\text{III}}(\text{bpy})_2(\text{OH}_2)]^{4+}$ (**19**, Figure 4), the first well-characterized molecular WOC ever reported (Gersten et al., 1982), research initially focused on developing dinuclear Ru-WOCs, designed to favor O–O bond formation *via* intramolecular interaction of two metal-oxo (I2M) fragments (Romain et al., 2009). Although this design principle has sometimes proven flawed, since some dinuclear catalysts actually lead to O–O bond formation *via* water nucleophilic attack (WNA) at a single Ru=O center (Cape and Hurst, 2008; Liu et al., 2008; Romain et al., 2009; Neudeck et al., 2014) or other more peculiar pathways (Ertem and Concepcion, 2020), it provided some interesting catalyst families like those featuring 3,5-bis(2-pyridyl)pyrazolate (Sens et al., 2004) and rigid polypyridyl (Zong and Thummel, 2005; Xu et al., 2010; Kagalwala et al., 2021) ligands. Complexes **20** and **21**, reported

by the groups of Llobet and Thummel respectively, are two notable examples of such a class of catalysts. **20** catalyses the oxidation of water to molecular oxygen driven by CAN with a TOF value of 0.014 s^{-1} and TON of 512, whereas **21** showed a higher TOF value of 0.046 s^{-1} and a TON of 538 under similar conditions.

An important breakthrough in the field occurred in 2005, when Thummel and coworkers reported for the first time a series of mononuclear Ru complexes displaying water-oxidation activity (Zong and Thummel, 2005). In particular, the complex **22** with the methyl substituent showed the best performances reaching a TOF value of 0.014 s^{-1} and TON of 580 using CAN as sacrificial oxidant. Since then, the growing awareness that "one site is enough" (Concepcion et al., 2008) allowed to speed up Ru-catalyst development by focusing on simpler monomolecular species. Pyridyl based ligands were widely used (Wasylenko et al., 2010; Yagi et al., 2011; Kaveevivitchai et al., 2012; Kimoto et al., 2012; Tamaki et al., 2014). However, significant improvement in the catalytic activity for water oxidation was not achieved until the introduction of carboxylate-containing ligands into the catalyst structure, lowering the oxidation potential of Ru(II) to Ru(III). The family of Ru-bda catalysts, introduced by the group of Sun (Duan et al., 2009, 2012; Zhang and Sun, 2019b), is a most notable example (bda = 2,2'-bipyridine-6,6'-dicarboxylate). Complex **23** with the methyl substituent exhibits good catalytic performances in WO driven by CAN (Wang L. et al., 2012), and under electro- and photochemical conditions (Duan et al., 2010). The stabilizing effect of the introduced anionic carboxylate fragments appeared crucial to obtaining high activities (TON of 2000 and TOF of 41 s^{-1} using CAN as SO and 180 mV overpotential in electrocatalytic WO) (Duan et al., 2009; Wang et al., 2012b).

Several bda-ligand variations have been proposed to tune the redox properties of the metal center and/or the relay properties of the ancillary ligand (Matheu et al., 2015; Shaffer et al., 2017; Zhan et al., 2019; Vereshchuk et al., 2020; Yang et al., 2021). In particular, in complex **24** the use of phosphonate rather than carboxylate groups allowed to achieve a record TOF of 16000 s^{-1} at pH = 7 with an overpotential of 530 mV (upon *in situ* ligand oxidation) (Vereshchuk et al., 2020). Also the axial ligands have drawn significant attention, due to their ability to facilitate Ru=O coupling by establishing intermolecular π - π stacking (Duan et al., 2013; Richmond et al., 2014; Wang et al., 2014; Creus et al., 2016; Fan et al., 2016; Xie et al., 2018) or, in some specific cases, electrostatic (Yi et al., 2021) interactions.

It should be noted, however, that such astonishingly high activities are often obtained at rather high catalyst concentrations, in the order of 10^{-3} – 10^{-5} M , to minimize the kinetic limitations of the bimolecular I2M mechanism that is characteristic of this catalyst class. Interestingly, Sun and coworkers have recently shown that the use of asymmetrically substituted pyridine axial ligands improves π - π stacking interactions, mitigating concentrations effects on activity; for instance, the TOF of the 3,4-dibromopyridine catalyst **25** drops from 460 s^{-1} at $[\text{Ru}] = 100 \mu\text{M}$ to a still noticeable TOF of 31 s^{-1} at $[\text{Ru}] = 1 \mu\text{M}$ in CAN-driven OER (Timmer et al., 2021). Alternative and more elaborate

strategies have been proposed, for instance, by Reek and coworkers who exploited self-assembled nanospheres to increase local catalyst concentration (Yu et al., 2018). High activities at low concentrations can be achieved also with supramolecular Ru-bda macrocycles, following a WNA rather than I2M mechanism for reasons that remain to be fully understood and possibly related to the reduced mobility of the metal complexes in solution (Schulze et al., 2016).

The development of Ir-WOCs has been at least as prolific as that of Ru-based ones (Thomsen et al., 2015). Even though the first example, reported by Bernhard and coworkers in 2008, features two phenylpyridine ligands coordinated at an octahedral metal center (complex **26**) (McDaniel et al., 2008), the evolution of molecular Ir-WOCs has mostly focused on *pseudo*-tetrahedral Cp^{*}-complexes, first reported by Crabtree and coworkers in 2009 (Hull et al., 2009). A plethora of Ir-Cp^{*} complexes with (mostly bidentate) ligands has been proposed as water oxidation catalysts. To name but a few, these include complex **27** bearing the 2-(2'-pyridyl)-2-propanolate (pyalc) ligand proposed by Crabtree and coworkers (Sharninghausen et al., 2016; Yang et al., 2016; Michaelos et al., 2017), complexes **28**, **29** and **30** with different carbene ligands introduced by the groups of Albrecht, Bernhard and Hetterscheid (Lalrempuia et al., 2010; Hetterscheid and Reek, 2011; Venturini et al., 2014; Woods et al., 2014; Navarro et al., 2018; Vivancos et al., 2018), and complex **31** bearing the pyridine-carboxylate (pica) fragment introduced by Macchioni and coworkers (Bucci et al., 2012; Menendez Rodriguez et al., 2017a; Van Dijk et al., 2020; Rodriguez et al., 2021).

Comparing activity of these systems is difficult, as discussed above. Rather few electrochemical studies have been reported for molecular Ir-WOCs. The simple [Cp^{*}Ir(H₂O)₃]²⁺ (**32**) (Blakemore et al., 2011), as well as many other Cp^{*} and non-Cp^{*} catalysts (Van Dijk et al., 2020), easily undergo degradation to oxide nanoparticles under electrochemical OER conditions. Yet, **27**, having a strongly electron donating and oxidation resistant pyridine-alkolate ligand, was found to remain homogenous under electrocatalytic WO conditions up to 680 mV overpotential (Schley et al., 2011), although some particle formation has been observed in chronoamperometric studies at higher potentials (670 mV) (Van Dijk et al., 2020). Also some pyridyl-triazolylidene Ir-WOCs remain molecular entities and deliver a stable 120 μA current at 1.8 V vs. RHE; only minor decomposition to catalytically inactive nanoparticles occurs (Olivares et al., 2020).

Catalytic performances in WO driven by sacrificial oxidants have been more widely explored, and some benchmarking studies are available with both CAN (Koelewijn et al., 2016) and NaIO₄ (Menendez Rodriguez et al., 2017b). In particular, the most active molecular Ir-WOCs in combination with NaIO₄ appear to be the simplest [Cp^{*}Ir(H₂O)₃]²⁺ (TOF = 7 s⁻¹ in NaIO₄-driven WO) and [Ir(OH)₆]²⁻ (TOF = 9 s⁻¹), (Menendez Rodriguez et al., 2017b), even though the actual molecular vs. heterogeneous nature of the latter species has been debated (Savini et al., 2010; Hintermair et al., 2012; Menendez Rodriguez et al., 2017b).

This observation relates to a key issue in Ir-catalyzed WO, that is, the identification of the active species. Several spectroscopic studies revealed that catalyst activation involves *in situ* oxidative degradation of the Cp^{*} (Savini et al., 2011; Wang et al., 2012a; Hintermair et al., 2013; Ingram et al., 2014; Zuccaccia et al., 2014; Sharninghausen et al., 2016; Yang et al., 2016). This leads to small molecules like acetic and formic acid, which are released in the reaction medium, and oxygenated fragments like substituted acetylacetonates, which likely remain coordinated at iridium. Strong experimental evidence supporting the latter hypothesis has been reported in a recent catalytic study on differently substituted Cp'-WOCs, demonstrating that intrinsic catalyst activity depends on the substituent on the Cp' fragment (Gatto et al., 2021).

The fate of the non-Cp^{*} ligands is far less explored. The above mentioned ligands are more oxidation resistant than Cp^{*} and often assumed to remain coordinated at iridium during catalysis (Sharninghausen et al., 2016; Yang et al., 2016; Hu et al., 2021). However, as elegantly demonstrated by Fukuzumi and coworkers, even robust ligands like bipyridine can undergo decomposition if decorated with attackable substituents like-OH (Hong et al., 2012). Furthermore, albeit not degraded under OER conditions, differently substituted X-pica ligands likely detach from iridium upon catalyst activation (Rodriguez et al., 2021); this implies that [Cp^{*}Ir(X-pica)]⁺ complexes lead to the same active species formed with the simpler [Cp^{*}Ir(H₂O)₃]²⁺, with variations in catalytic activity being determined by the ease of ligand detachment. It remains to be proven whether this applies also to other types of ancillary ligands, but it is worth mentioning that this might explain the difficulties in developing Ir-WOCs more active than [Cp^{*}Ir(H₂O)₃]²⁺.

Along with Ru and Ir, several WOCs based on earth-abundant elements have been reported (Kärkäs and Åkermark, 2016; Lloret-Fillol and Costas, 2019; Kondo et al., 2021; Zhang et al., 2021). Initially, efforts focused on Mn (Najafpour et al., 2016), aiming at mimicking the Mn/Ca cubane active complex of natural Photosystem II (Kanaby et al., 2011; Kanady et al., 2014). Then, other elements have drawn significant attention, such as Co (Artero et al., 2011; Du and Eisenberg, 2012), Ni (Du and Eisenberg, 2012; Hessels et al., 2020a), Cu (Lee et al., 2020), and Fe (Du and Eisenberg, 2012; Casadevall et al., 2019; Liu et al., 2019). Herein, the most extensively studied metal, iron, is discussed as representative case.

Despite some early indications in the 1980s (Elizarova et al., 1981), the search for Fe-WOCs sparked in 2010 with the report on iron-centered tetraamido macrocyclic ligands (Fe-TAML) by Bernhard and Collins (Ellis et al., 2010). Among all, complex **33** exhibits the highest activity but very poor durability (TOF = 1.3 s⁻¹; TON = 10), which could be somewhat improved using a Biuret-Modified ligand (TOF = 0.8 s⁻¹; TON = 220 under photochemical conditions) (Panda et al., 2014).

The larger family of well-defined Fe-WOCs is based on non-heme, multidentate aminopyridine ligands (Codolà et al., 2013, 2019; Zhang B. et al., 2014; To et al., 2015; D'Agostini et al., 2021). For instance, complex **34** bearing the *N,N'*-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine (mcp) ligand have proved to be rather stable against decomposition in chemically driven

WO (Fillol et al., 2011), but also under electrochemical conditions with an onset overpotential of 0.47 V (D'Agostini et al., 2021). 1-(2'-pyridylmethyl)-1,4,7-triazacyclononane (pytacn) ligands have been widely studied showing how activity increases with electron withdrawing substituents in para position of the pyridine ring and non-hindering substituents in ortho (Codolà et al., 2013; D'Agostini et al., 2021). Complex **35** bearing the nitro substituted pyridine showed the best performances in this series with a TOF of 0.23 s⁻¹ and TON of 180. Importantly, in order to be active, all these Fe(NNN) complexes require the two labile ligands to be in *cis*-position with each other, as nicely demonstrated by Hetterscheid and co-workers by comparing *cis*-[Fe (cyclam) Cl₂]Cl (cyclam = 1,4,8,11-tetraazacyclotetradecane; **36**), which catalyzes WO at 0.47 V overpotential, and its *trans*-analogue, which is inactive in OER (Kottrup and Hetterscheid, 2016).

Aiming at improving the stability of high valent intermediates, Meyer and coworkers also proposed to use anionic rather than neutral tetradentate ligands, like bis(pyridine-2-ylmethyl)]amino-N-quinolin-8-yl-acetamido. The resulting complex **37** was found to be an effective electrocatalyst in propylene carbonate–water mixtures (Coggins et al., 2014), but not in aqueous solutions (Zhang B. et al., 2014).

Di- or even multi-metallic catalysts have been reported as well, aiming at facilitating the rate-limiting O–O bond formation as discussed above for Ru-WOCs (Panda et al., 2014; Das et al., 2016; Okamura et al., 2016; Kottrup et al., 2018). These include, for instance, the iron-tetrapyridyl electrocatalysts **38** and **39**, first reported by the group of Tummel (Wickramasinghe et al., 2015), exhibiting some of the lowest overpotentials among Fe-WOCs of 300–400 mV (Wickramasinghe et al., 2015; Kottrup et al., 2018).

CONCLUDING REMARKS AND OUTLOOK

The versatility of molecular catalysts clearly emerges from the results summarized in the above sections. In particular, it appears evident that ancillary ligand modification represents an effective handle for properties tuning, which still offers large possibilities for further improvement. Establishing straightforward structure-properties correlations remains arduous at this stage, the main hurdle being the limited understanding of reaction mechanisms and (pre)catalyst speciation. Nevertheless, some successful examples of ligand tailoring might help orienting future research, like DuBois' aza-diphosphino cyclic ligands with their proton relay properties (Helm et al., 2011) or the axial ligands establishing π - π stacking interactions in Ru-bda catalysts (Duan et al., 2013; Richmond et al., 2014; Wang et al., 2014; Creus et al., 2016; Fan et al., 2016; Xie et al., 2018). Increasing the currently very limited number of systematic catalyst screenings to buildup robust and consistent experimental databases is essential in this respect (Garrido-Barros et al., 2017; Craig et al., 2019; Craig and García-Melchor, 2021; Kondo et al., 2021). Improving activity/lowering the necessary overpotential is still an open challenge in HER and especially in OER. Nevertheless, it should be emphasized that rather high maximum TOFs are now accessible with the latest generation catalysts, and it is reasonable to expect that ligand design can quite easily lead to

further improvement. Indeed, rather than catalytic activity, the biggest challenge for molecular catalysts regards stability (Limburg et al., 2012).

OER is more problematic than HER in this respect, due to the harsher reaction conditions needed in the former case. *In situ* ligands modifications are very common under the strongly oxidative reaction conditions necessary for both chemical and photo/electrochemical WO. Often, they are functional to the generation of the active species, as in the above discussed case of Ir-WOCs (Savini et al., 2011; Wang et al., 2012a; Hintermair et al., 2013; Ingram et al., 2014; Zuccaccia et al., 2014; Sharninghausen et al., 2016; Yang et al., 2016; Gatto et al., 2021), but also for ruthenium (Liu et al., 2014, 2018; López et al., 2014; Akhtar et al., 2016; Kagalwala et al., 2017; Vereshchuk et al., 2020) and earth-abundant catalysts (Hong et al., 2013; Kottrup and Hetterscheid, 2016; Codolà et al., 2019). In many other cases, however, they are strongly detrimental, typically leading to the formation of metal oxide nanoparticles. A relevant example is the pentanuclear iron complex reported by Masaoka and coworkers in 2016 (Okamura et al., 2016), whose catalytic activity was later attributed to iron oxide material deposited on the electrode surface (Pelosin et al., 2020). This is extremely problematic for earth-abundant WOCs (Chen et al., 2013; Parent et al., 2014; Hessels et al., 2020b), but certainly non-negligible also in the case of noble metals (Depasquale et al., 2013; Lewandowska-Andralojc et al., 2014; Van Dijk et al., 2020). The use of strongly electron donating, polydentate ligands has proven effective in mitigating this problem for Fe-WOCs (Casadevall et al., 2019), and similarly positive results have been obtained, for instance, with the pyalc ligand for Ir-WOCs (Schley et al., 2011); yet, catalyst stability remains difficult to optimize and still unsatisfactory for commercial applications.

It is worth emphasizing here that preventing and/or understanding catalyst *in situ* modifications would also facilitate the identification of rational design principles. The abovementioned results on Cp*Ir-WOCs probably represent a most advanced, yet still intricate, case in this respect. By combining the information derived from several spectroscopic and kinetic studies (Savini et al., 2011; Wang et al., 2012a; Hong et al., 2012; Hintermair et al., 2013; Ingram et al., 2014; Zuccaccia et al., 2014; Sharninghausen et al., 2016; Yang et al., 2016; Gatto et al., 2021; Hu et al., 2021; Rodriguez et al., 2021), some important hints on the structure of the active species emerge: it is likely a multimetallic oxo-species containing fragments deriving from Cp* oxidative degradation and, at least in most cases, no other ancillary ligands of the parental precatalysts (Yang et al., 2016; Gatto et al., 2021; Rodriguez et al., 2021). This hypothesis of a multimetallic, possibly nanocluster, active species calls for a strong integration of homogenous and heterogeneous catalysis approaches (Li et al., 2021).

Regarding the applications of molecular catalysts, another important aspect to consider is the integration of these systems in photo/electrochemical devices for large scale hydrogen production. All the above discussed examples refer to molecular catalysts in homogenous phase in laboratory scale experiments, but these conditions can be hardly applied in industrial plants. First, the use of a molecular catalyst in

electrolytic solution would be limited by only a small fraction of the catalyst being active in the diffusion layer around the electrode. Second, it would hamper the recovery and recycle of active metal, which is particularly important for noble metals.

Effective strategies for the heterogenization are therefore needed for molecular catalysts to become suitable for commercial applications (Materna et al., 2017; Rosser and Reisner, 2017; Zhang and Sun, 2019a; Macchioni, 2019; Zahran et al., 2019; Xiao et al., 2021; Yi et al., 2021). They require elaborate optimization of the composition, morphology and particle size of the support, as well as engineering of the ancillary ligand for anchoring the organometallic complex; compatibilization with the electrode material is another critical aspect.

Several notable examples of heterogenized catalysts have been reported in both HER and OER. To name but a few, Artero and coworkers effectively grafted a diimine–dioxime cobalt complex onto the surface of a carbon nanotube electrode, catalyzing HER with a TON of 55000 at an overpotential of 350 mV in aqueous solutions (Andreiadis et al., 2013); even better performances were obtained with a nickel bisdiphosphine catalyst supported on multiwalled carbon nanotubes, reaching 100,000 turnovers at 20 mV overpotential in aqueous sulfuric acid solution (Alan et al., 2009). Alternative supports have also been reported, like metal organic surfaces (Clough et al., 2015). In OER, metal oxide supports are commonly used, and proved successful for instance in combination with a dimeric Ir-pyalc catalyst (TON $>1 \times 10^6$ at 250 mV overpotential) (Sheehan et al., 2015), Ir-bipyridine (TON $>5 \times 10^5$ and TOF $>6.7 \text{ s}^{-1}$ at 280 mV overpotential) (Joya et al., 2012) catalysts. Also IrCp*-N-

dimethylimidazolin-2-ylidene catalysts immobilized on a polycrystalline gold electrode exhibited good stability with a TOF of 2.9 s^{-1} at an applied overpotential of 430 mV (Diaz-Morales et al., 2014). It is worth mentioning that molecular catalysts can be also used to enhance the performance of photoactive materials like BiVO₄ (Wan et al., 2018) and WO₃ (Klepser and Bartlett, 2014), or simply serve as well-defined precursors for the controlled deposition of metal atoms in the electrode surface.

These examples show how integrating molecular complexes with suitable supports represents a frontier in catalysis for water splitting. The close cooperation between material scientists and organometallic chemists will guarantee significant progress in this field.

AUTHOR CONTRIBUTIONS

AM designed the review discussing it with all authors. AM and FZ wrote most of the paper. All authors contributed in finding relevant literature results to illustrate in the paper.

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