Molybdenum-Containing Metalloenzymes and Synthetic Catalysts for Conversion of Small Molecules

Donghyeon Kim, Jaeheon Lee and Junhyeok Seo *

Department of Chemistry, Gwangju Institute of Science and Technology, Gwangju 61005, Korea; kdhhdh934@gist.ac.kr (D.K.); jaeheonlee@gist.ac.kr (J.L.)
* Correspondence: seojh@gist.ac.kr

Abstract: The energy deficiency and environmental problems have motivated researchers to develop energy conversion systems into a sustainable pathway, and the development of catalysts holds the center of the research endeavors. Natural catalysts such as metalloenzymes have maintained energy cycles on Earth, thus proving themselves the optimal catalysts. In the previous research results, the structural and functional analogs of enzymes and nano-sized electrocatalysts have shown promising activities in energy conversion reactions. Mo ion plays essential roles in natural and artificial catalysts, and the unique electrochemical properties render its versatile utilization as an electrocatalyst. In this review paper, we show the current understandings of the Mo-enzyme active sites and the recent advances in the synthesis of Mo-catalysts aiming for high-performing catalysts.

Keywords: molybdenum; metalloenzymes; FDH; CODH; nitrogenase; homogeneous; heterogeneous electrocatalysts; HER; OER

1. Introduction

Fixation of atmospheric nitrogen to ammonia has been promoted by the Haber–Bosch process, and the capacitated mass production of foods accelerated the increase of the world population [1,2]. The rapid growth of fossil fuel-based industry unavoidably increased atmospheric CO$_2$, and resultantly aggravated the global warming and climate crisis. To suggest solutions for those anthropogenic issues and mitigate the current environmental problems, scientific progress to convert fossil fuel-based energy systems toward sustainable ways is keenly desired along with other social and economic efforts [3]. In the line of scientific cognition, we review catalysts for energy conversion reactions including small molecules such as CO$_2$, N$_2$, H$_2$, and O$_2$ as reactants or products. Numerous catalysts have been developed in recent decades owing to the high interest in energy conversion reactions [4–8]. Mo ion is found to be an essential component in biological catalysis [9], as well as a very promising metal candidate among Earth-abundant metals for applications to electrocatalysts and photocatalysts [4,10,11]. Herein, we review versatile utilization of Mo ions in natural and synthetic catalysts.

Mo-containing homogeneous catalysts utilize both low- and high-valent Mo ions, whereas metalloenzymes and their model complexes have high-valent Mo centers. Except for FeMo-nitrogenase [12], Mo-enzyme active sites always use dithiolene ligation of the molybdopterin (MPT) moiety to stabilize a Mo(IV/VI) ion during the redox reaction and to assist electron transfer between metal and ligand [13]. Moreover, the chalcogenide ligand and nearby amino acid play essential roles to determine the selective reactivity of Mo active sites. Although enzyme mechanisms remain unclear despite significant interests, ligand identity and coordination structures seem to be critical factors to determine catalytic activity. We can propose synthetic routes for the design of new Mo-based catalysts from comparing structures, properties, and reactivities of metalloenzymes and artificial catalysts [14]. Although relatively less studied, Mo-clusters have shown promising electrocatalytic activities due to their intermediate behaviors between metal-coordination...
complexes and nanoparticle catalysts [15]. In the perspective of developing efficient electrocatalysts, Mo-nanomaterials, which have shown remarkable electrocatalytic activities, should be considered together. Preparation methods of Mo-nanomaterials determine their catalytic activities, and proximal atoms and electronic conditions around Mo ions are closely related to reactivities of surficial Mo ions [16,17].

2. CO₂ Electrocatalysts

Considering current energy systems, a drastic diminution of fossil fuel consumption seems unrealistic. However, continuous research for recycling anthropogenic CO₂ will be able to provide feasible solutions to current energy and climate issues. Among various CO₂ transformation methods, electrochemical conversion of CO₂ may be an attractive way to be conjugated with solar/electric energy conversion reactions [18]. Mo-enzymes of the formate dehydrogenases [19] (Mo-FDH) and the carbon monoxide dehydrogenases [20] (MoCu-CODH) are the most efficient CO₂-catalysts on Earth, and their synthetic models are known, albeit short of the enzyme activity [21]. Moreover, many homogeneous and heterogeneous catalysts have been developed for CO₂ conversion reactions.

2.1. Metalloenzymes with CO₂ Reactivity

2.1.1. Formate Dehydrogenases

Formate dehydrogenases (FDHs) is a group of metalloenzymes that catalyze a reversible conversion of formate to CO₂. The CO₂ reactivity of the FDH active site has obtained research interests because the enzyme functions near the potential of −420 mV vs. NHE (Normal hydrogen electrode) scarcely requiring overpotential. It is known that the reaction rate is varied by bacteria. *Rhodobacter capsulatus* FDH facilitates oxidation of formate to CO₂ at a rate of 36.5 s⁻¹ and the reverse direction at a rate of 1.6 s⁻¹ [22]. *Desulfovibrio desulfuricans* FDH oxidized formate much more quickly at 543 s⁻¹ and reduced CO₂ at 46.6 s⁻¹ [23]. The FDH reactivity is directly related to the active site structure, which has a Mo center surrounded by two pyranopterin-conjugated dithiolene ligand, a chalcogenide (hydroxide or sulfide) ligand, and SeCys amino acid as a sixth ligand (Figure 1). In addition, additional roles of adjacent amino acids such as Arg and His seem to be important to assist the FDH reaction by stabilizing reaction intermediates.

\[
\text{CO}_2 + 2e^- + H^+ \rightleftharpoons \text{HCOO}^-, \quad E' = -420 \text{ mV}
\]

![Figure 1. Oxidized form of the FDH active site from *Escherichia coli* (PDB 2IV2).](image-url)

In 1997, Boyington and coworkers first reported the crystal structure of *E. coli* FDH [24]. Later, in 2006, Raaijmakers and coworkers reinterpreted the crystal structure and proposed a reaction pathway of the FDH active site (Scheme 1) [25]. They suggested that SeCys is reversibly bound to the Mo center during the redox reactions so that offers a vacant site
to interact with substrates. Once formate bound to Mo$^{6+}$ site, a proton migrated to His residue, and CO$_2$ was released along with the reduction of Mo$^{6+/4+}$ site. If two electrons were transferred to [4Fe4S] cluster, SeCys recombined at the Mo site. In the proposed reaction, the sulfide ligand did not participate in the reaction.

In 1997, Boyington and coworkers first reported the crystal structure of FDH from E. coli. They suggested a direct interaction of formate with Mo center based on X-ray absorption spectroscopy. When azide entered in the Mo-S bond, the azide entered between Arg/His and Mo=S, not at the binding site of SeCys (Scheme 3).

The same group proposed that a hydride transfer occurred in the conversion of Mo(VI) = X and Mo(IV)-XH, and the formate oxidation would likely occur as an indirect pathway [23]. In a substitution experiment of Mo-bound formate for isoelectronic azide, the azide entered between Arg/His and Mo=S, not at the binding site of SeCys (Scheme 3).

Haumann and coworkers reported that the Mo=S bond length of the oxidized form is $\sim$2.16 Å on the basis of X-ray absorption spectroscopy [26]. They suggested that Mo-SH possibly exists based on the Mo-S distance of $\sim$2.4 Å in the X-ray crystal structure and SeCys stays apart from the Mo center during the reaction. They suggested a direct interaction of formate with Mo center based on X-ray absorption spectroscopy. When azide entered in the Mo-SeCys site of the oxidized form, a thiocarbonate intermediate was formed with the dissociation of the S-SeCys bond, and adjacent Arg$^+$ amino acid possibly stabilized the negatively charged intermediate. The roles of nearby amino acids seemed to be critical for the catalytic reaction at the active site [26,27].

Scheme 1. A reaction pathway proposed by Raaijmakers.

Another reaction pathway including the role of sulfide ligand has been proposed (Scheme 2). In 2011, Moura and coworkers suggested that the sulfide ligand assists the reversible dissociation/association of Mo-SeCys bond on the basis of theoretical studies. A probable Mo-S-SeCys intermediate could open a coordination site to interact with formate. Once a proton migrated from formate to SeCys, a thiocarbonate intermediate was formed with the dissociation of the S-SeCys bond, and adjacent Arg$^+$ amino acid possibly stabilized the negatively charged intermediate. The roles of nearby amino acids seemed to be critical for the catalytic reaction at the active site [26,27].

Scheme 2. A reaction pathway including the role of sulfide ligand.
the Mo-Cys bond distance decreased. Conversely, when azide was removed, the Mo-Cys distance increased [29].

Scheme 3. Indirect reaction pathway through Mo-SH and Arg interaction.

The reaction mechanism of the FDH active site is a continuous research topic because an in-depth understanding of the active site will lead to the development of efficient electrocatalysts for CO₂ conversion.

2.1.2. MoCu-Carbon Monoxide Dehydrogenases

In 2002, MoCu-carbon monoxide dehydrogenase (CODH) from *Oligotropha carboxidovorans* was found to catalyze the oxidation of CO to CO₂ under aerobic conditions. The enzyme exists as a dimer form of heterotrimer [30]. The hetero-trimer is composed of 88.7 kDa L (809 residues), 30.2 kDa M (288 residues), and 17.8 kDa S (166 residues). The L subunit contains molybdopterin-cytosine dinucleotide (MCD), and the M subunit has a flavin adenine dinucleotide (FAD) cofactor. Two [2Fe-2S] clusters stay in the S subunit [31]. As characterized by X-ray crystallography and extended X-ray absorption fine structure (EXAFS), the MoCu-CODH active site is composed of a hetero-bimetallic cluster of (MCD)Mo^{VI}(\mu^{2}-S)-Cu(S-CYS), and the bent $\mu^{2}$-S bridge connects the Cu and Mo center (Figure 2a) [32]. The resting state of the active site was characterized as a Mo^{VI}(O)₂SCu¹ core, and the catalytic oxidation possibly occurs with CO binding at the Cu center.

In 2002, Dobbeck and coworkers reported the X-ray structure of the MoCu-CODH with N-butylisocyanide, where the N-butylisocyanide entered between $\mu$-S–Cu bond by cleaving the bridging sulfide bond [31]. Accordingly, they suggested that CO would interact with the active site in a similar way as the isoelectronic molecule as forming a $\mu$-thiocarbamate intermediate (Figure 2b).

However, Siegbahn and coworker suggested that CO binding to Cu is energetically favored from the computational studies. Next, the Cu-CO likely experiences a nucleophilic attack by the equatorial Mo=O to form a thiocarbamate intermediate, and CO₂ can be released with coordination by H₂O or (–OH) (Figure 2c) [33].

The formation of a thiocarbamate intermediate was suggested previously, but Hofmann and coworkers claimed that a thiocarbamate intermediate is not relevant to the MoCu-CODH catalytic cycle, because a thiocarbamate moiety is too stable to be involved in the catalytic steps (Figure 2d) [34]. Hille and coworkers also proposed that the Cu-CO-O-Mo bond is formed after CO insertion (Figure 2e). They emphasized the role of nearby Glu763 residue to deprotonate H₂O. A nucleophilic attack of –OH to the labile equatorial Mo=O could promote the release of CO₂ [30] The aerobic MoCu-CODH catalyzed CO oxidation with $k_{cat}$ 93.3 s⁻¹ at pH 7.2 condition [35].

2.2. Structural Analogs of CO₂ Enzymes

2.2.1. FDH Analogs

The high efficiency of the FDH enzyme spurs researchers to synthesize structural analogs of the enzyme active site. Synthetic procedures for various dithiolene complexes enabled modeling studies of the enzyme active site having the Mo-bis(dithiolene) moiety. High-valent Mo(IV-VI)-bis(dithiolene) appeared to be highly reactive. Although the Mo enzyme active site is protected by surrounding proteins, the air-sensitivity of high-valent Mo in solution conditions makes the modeling study difficult. On the other hand, the high reactivity could be a clue to the CO₂ reactivity of the Mo site. Previous studies
have revealed that the selective reactivity of Mo-bis(dithiolene) complexes is related to auxiliary ligands.

Figure 2. (a) MoCu-CODH active site (O. carboxidoxorans CODH, PDB code 1N5W) and reaction pathways proposed by (b) Dobbek, (c) Siegbahn, (d) Hofmann, and (e) Hille.

The Mo-FDH and W-FDH active sites have very similar coordination environments except for the metal center, although their reaction conditions are different because of the bacterial habitat. In 2012, Kim and Seo reported CO₂ reactivity of the in-situ generated [WIV(OH)(S₂C₂Ph₂)]− (2) [36] as an example of the functional model of the W-FDH active site (Scheme 4) [25]. Complex 2 generated by hydrolysis of [WIV(OPh)(S₂C₂Ph₂)]− (1) [37,38] showed the CO₂ reactivity at mild condition, and it was suggested that a nucleophilic attack of –OH to CO₂ formed a W-(bi)carbonate intermediate. Although the model complex did not show a catalytic activity, the plausible formation of a W-(bi)carbonate intermediate was similar to the reactivity of the FDH active site [26]. They also reported a stoichiometric reduction of CO₂ to formate by [WIV(O(S₂C₂Me₂)]2− (3) at 90 °C [39]. A W-carbonate intermediate was suggested as an intermediate before the CO₂ reduction, but the oxidized W complex was dimerized to [WIV₂O₂(μ-S)(μ-S₂C₂Me₂)(S₂C₂Me₂)]²− (4) at the high temperature as frustrating catalytic reaction (Scheme 4).

Fontecave and coworkers reported catalytic CO₂ reduction by Ni-bis(dithiolene) complex using a dithiolene derivative of quinoxaline-pyran-fused dithiolene (qpdt²⁻), which is similar to the molybdopterin (MPT) structure of the FDH active site (Scheme 4) [40]. In 2018, they used the qpdt²⁻ ligand to prepare Mo complexes, MoIVO(qpdt)₂ (5), [MoIVO(H-qpdt)₂]²⁻ (6), and [MoIVO(2H-qpdt)₂]²⁻ (7), as the Mo-FDH models, and examined the photocatalytic CO₂ reduction activity [41]. The reduced forms of H-qpdt and 2H-qpdt had similar oxidation states with the MPT. Using [Ru(bpy)₃]²⁺ photosensitizer, 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzoimidazole as a sacrificial electron donor in the solution of
triethanolamine and acetonitrile (1:5), and irradiation with a 300 W Xe lamp on the Mo complex solutions afforded CO2-derived products (CO and HCO2H) and H2. Complex 5 gave the CO2-reduction products with 19% and mostly H2 (81%). However, complex 6 increased the CO2-reduction yield to 47%, and complex 7 provided the CO2-reduction products in the highest yield of 58% with over 100 turnover number (TON) for 68 h.

Scheme 4. FDH model complexes.

Structural and functional analogs of the FDH active sites have been reported with rare examples; however, the catalytic activities remain much less than the enzymes. Secondary coordination ligands mimicking amino acids surrounding the enzyme active site would give new catalyst designs to achieve similar activities as the enzyme.

2.2.2. MoCu-CODH Analogs

In 2020, Mougel and coworkers synthesized [(bdt)Mo(O)S2CuCN]2− (8) (bdt = benzenedithiolate) as a MoCu-CODH model complex (Scheme 5) [42]. The Mo and Cu were bridged by μ2-sulfide ligand as the enzyme active site, and a bdt ligand was used to model the MPT. Complex 8 showed a catalytic reduction peak at E1/2 = −2.07 V vs. Fc+/Fc in CO2-saturated acetonitrile. Controlled potential electrolysis (CPE) at −2.62 V vs. Fc+/Fc in the presence of 0.1 M 2,2,2-trifluoroethanol (TFE) produced the reaction products of formate (Faradaic efficiency (FE) = 69%), CO (8%) and H2 (19%). It was a rare example to describe the MoCu-CODH model with the CO2 reduction activity, although the MoCu-CODH enzyme previously showed only the CO oxidation activity [20].

Scheme 5. MoCu-CODH active site and the model complex.

2.3. Synthetic Electrocatalysts for CO2 Reduction

2.3.1. Homogeneous Mo Complexes for CO2 Reduction

In 1978, Reichert and coworkers reported the CO2 reactivity of a dinuclear Mo2(OEtBu)6 (9) [43]. Two CO2 molecules were reversibly inserted into the Mo-OEtBu bonds to form Mo2(O2COEtBu)2(OEtBu)4 (Scheme 6) (10). From the X-ray structure, the Mo-Mo triple bond, bridged by two O2COEtBu, was measured to be 2.241 Å. The CO2 insertion occurred in both the solid and liquid states of the complex, and sublimation of the CO2 adduct at 100 °C afforded back the complex 9 by releasing CO2.
Metal ligand cooperation (MLC) is a useful method to fixate CO2. The trans-Mo(C2H4)2(PMe3)4 (11) reacted with CO2 under mild conditions [44], where CO2 was inserted into Mo-ethylene bond to form a Mo-acrylate moiety in \([\text{Mo(H}_2\text{CCHCO}_2\text{H})\text{(C}_2\text{H}_4\text{)}\text{(PMe}_3\text{)}_2]\) (Scheme 7) (12). The acrylate frequency was measured as 1500 cm\(^{-1}\) and the \(^{13}\text{C}\) NMR (Nuclear magnetic resonance) chemical shift at 175–180 ppm. Complex 11 reacted with a stoichiometric amount of CO2 under 1 atm to give 12, which could be converted back to 11 by treatment of n-BuLi under H\(_2\) with concomitant LiO\(_2\)CCH\(_2\)CH\(_3\) product. In another MLC type reaction, a PNP-amide-assisted CO2 fixation was shown with Mo(NO)(CO)(PNP) (13) \((\text{PNP} = \text{N}(\text{CH}_2\text{CH}_2\text{PiPr}_2\text{)})\) [45]. Complex 13 converted stoichiometric amount of CO2 to formate in the presence of Na[N(SiMe3)2] and additional base of DBU, Et3N (Scheme 7). However, high pressure of CO2 (10 bar) and H\(_2\) (70 bar) was also required. The MLC method effectively lowered the binding energy of CO2 to Mo complex, but the formation of a highly stable ML-CO2 adduct rather prevented the catalytic cycle.

Interestingly, the same complex also promoted converse conversion of formic acid to CO2 shifted the reduction potential a bit negatively to −2.20 V vs. SCE. The addition of 1.6 M of TFE into the reaction mixture resulted in 149 TON per catalyst for 45 h in benzene containing triethylamine base.

Minato and coworkers synthesized a series of Mo-silyl hydrido complexes of \([\text{MoH}_3\text{[(Ph}_2\text{PC}_2\text{CH}_2\text{CH}_2\text{P(Ph)}\text{-C}_6\text{H}_4\text{-o}_2\text{][RSi-P,P,P,P,Si]}]]\) \((\text{R} = \text{Ph})\) (15a), \(\text{C}_6\text{F}_5\) (15b), 4-Me\(_2\)NC\(_6\)H\(_4\) (15c), cyclohexyl (15d), and n-C\(_6\)H\(_{13}\) (15e) [47]. Silyl ligands with a strong trans effect were employed to control the reactivity of the Mo center (Scheme 9) [48,49]. The RSi-Mo could make an open coordination site at trans position to allow binding of electrophilic molecules such as O\(_2\), CO\(_2\), and carboxylic acid. Under the reaction conditions of 2.0 M of dimethylamine, 30 atm of CO\(_2\), and 20 atm of H\(_2\), complexes 15a–e catalyzed the CO2 hydration as producing \(\text{NN,NDimethylformamide (DMF)}\) and H\(_2\)O. The catalytic conversion of CO2 to DMF could be controlled by the Si-substituent. The complex 15a with a Si-phenyl...
Interestingly, the same complex also promoted converse conversion of formic acid to CO2. Solutions generated only CO product as recording 1.0 s−1 TOF with 323 TON and 1.9 s−1 with 18b.

Scheme 9. Mo-silyl hydrido complexes.

Redox-active ligand could assist central metal ions for reductive CO2 reactions. Trovitch and coworkers have used bis(imino)pyridine ligand for hydrosilylations of ketones [50]. They synthesized (κ6-P,N,N,N,C,P-Ph2Pr-PDI)-MoH (17) (PDI = pyridine diamine) by a reduction of ((Ph2Pr-PDI)MoI) (16) with excess K/Hg (Scheme 10) [51]. Complex 17 reacted with CO2 under 0.2 atm of CO2 condition, where CO2 was inserted into Mo-H bond to form η1-formate-bound Mo(OC(O)H) species [52,53]. The Mo-formate 13C NMR resonance appeared at 169.7 ppm and the infrared (IR) frequency was detected at 1625 cm−1. Complex 17 also promoted a catalytic conversion of HBPin to H3COBPin and O(BPin)2 under 1 atm of CO2 as recording 40.4 h−1 turnover frequency (TOF) and 323 TON with consuming 97% of HBPin. Distillation of H3COBPin in water for 24 h generated MeOH, eventually producing 58% of MeOH starting from HBPin. They showed a potential pathway to convert CO2 to methanol. Kubiak and coworkers used bipyridine (bpy) ligands to prepare Mo-carbonyl complexes, Mo(bpy)(CO)4 (18a) and Mo(bpy-tBu)(CO)4 (18b) [54]. Complexes 18a and 18b showed electrocatalytic CO2 reduction activity in acetonitrile solution [55]. Complex 18a had a reversible redox couple at −1.58 V vs. SCE (saturated calomel electrode) and an irreversible wave at −2.14 V vs. SCE, and catalyzed CO2 reduction near the second reduction potential. Complex 18b shifted the reduction potential a bit negatively to −2.20 V vs. SCE. The addition of 1.6 M of TFE into the reaction solutions generated only CO product as recording 1.0 s−1 TOF with 18a and 1.9 s−1 with 18b.

Bernskoetter and coworkers used tertiary amine pincer type ligands to prepare CO2 hydrogenation catalysts [56]. Reduction of (PNMeP)MoCl3 with Na(Hg) under ethylene afforded (PNMeP)Mo(C2H4)2 (19), and the following oxidative C-H addition generated the Mo-H species of (PNCH2P)MoH(C2H4)2 (20) (Scheme 11) [57]. Blowing 4 equiv. of CO2 into complex 20 gave the Mo-О2CH moiety in complex 21. Catalytic production of formate was achieved by using LiOTF as cocatalyst and DBU base under 69 atm of H2 and CO2 (1:1 ratio) at 100 °C as recording 35 TON for 16 h.
hydrogenation catalysts [56]. Reduction of (PNMeP)MoCl3 with Na(Hg) under ethylene af-

Scheme 11. CO2 reactivity of (PNMeP)Mo(C2H4)2 complex.

The low-valent Mo complexes have shown promising activities for CO2, but the formation of relatively stable adducts or requirement of high-pressure conditions remain issues to solve for efficient catalyst development.

2.3.2. Heterogeneous Mo-Containing CO2 Reduction Electrocatalysts

In 1986, Frese and coworkers reported the reduction of CO2 to methanol using Mo electrode at the potential range of −0.57 to −0.67 V vs. SCE in CO2-saturated aqueous media (0.05 M H2SO4, pH 4.2) [58]. As a result, 18 μmol of methanol was obtained for 40 h with 50% FE together with 0.044 μmol of CO production.

MoS2 surface has shown CO2 reduction ability, but in general, the intrinsic properties such as poor electrical conductivity and few active sites cause low electrocatalytic activity. In 2014, Asadi and coworkers reported the layer-stacked MoS 2 nanomaterial [59]. The MoS2 surface conducted selective reduction of CO2 to CO in the presence of 4% 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF4) with a high reduction current of 65 mA/cm2 at −0.76 V vs. RHE (FE ~98%). The activity at a low overpotential (0.1 V) was measured to be 25 times higher than Au nanoparticles. They reported vertically aligned (VA) MoS2 with ~20 nm thickness by chemical vapor diffusion (CVD) method, and they went a further study with different VA-MoS2 with ~20 nm thickness by chemical vapor diffusion (CVD) method, and they also studied the metal-doping effect for the CO2 reduction activity [60]. The 5% Nb-doped VA-MoS2 began the CO2 reduction with onset overpotential of 31 mV, and it reached 237 mA/cm2 current density at −0.8 V vs. RHE. However, Ta-doped (3~18% Ta) VA-MoS2 showed 98~68 mA/cm2 at −0.8 V vs. RHE, which was rather lower than a pristine VA-MoS2 (121 mA/cm2).

Previously, Bi-deposited glassy carbon has shown a good catalytic activity for reduction of CO2 to CO because CO2− radical species are well stabilized on Bi site [61]. Interestingly, a formation of hetero-bimetallic MoBiSx (Mo/Bi 1:1) nanosheet showed different CO2 reduction product of methanol (FE 71.2%) with generation of side products of methane (7.8%) CO (9.6%) H2 (11.4%) [62]. It was observed that, if the Bi ratio was raised, the CO percentage increased. They explained that the further reduction process is probably promoted by the synergistic effect with MoS2-catalytically active for the proton reduction.

Nano-sized Cu particles have shown CO2-to-hydrocarbon electrocatalytic reduction activity [63]. The Cu-doping effect on the CO2 reactivity of MoS2 was studied by Yu and coworkers [64]. Flower-like MoS2 was prepared by hydrothermal method, and the surface was reacted with Cu(NO3)2·3H2O to give Cu/MoS2 composite with varying the Cu/Mo ratio. Specific Cu ratio (12.76%) exhibited four times higher catalytic current density at −1.7 V vs. SCE than a bare MoS2 as producing CO (FE = 35.19%), CH4 (17.08%), C2H4 (2.93%). The high Faradaic efficiency for CO2 reduction was because the surface-deposited Cu enhanced the electronic conductivity and CO2 adsorption ability of MoS2.

Few active sites have been an issue for the preparation of MoS2 electrodes, thus, synthetic methods are pursued to enlarge the MoS2 edge site area. Wang and coworkers used zeolitic imidazolate frameworks to prepare hollow MoS2 nanostructure, which effectively enlarged the exposed MoS2 edge area. The edge-exposed MoS2 was supported by N-doped carbon to improve electron transfer, which gave two times higher current density (34.31 mA/cm2 at −0.7 V vs. RHE) and 1.4 times higher FE (CO2-to-CO 93% FE) compared to MoS2 [65]. The N-doped carbon served as efficient conductive support, because the more
electronegative N atom decreases electron density at nearby carbon sites by improving electron transfer at the electrode surface. An enhanced surface electron transfer to MoS$_2$ edge could lower the energy barrier for the formation of CO$_2$ reduction intermediates on the catalytic site [66]. Zhu and coworkers prepared N-doped MoS$_2$ nanosheets on N-doped carbon nanodots (N-MoS$_2$@NCDs) through a solvothermal method [66]. N-MoS$_2$@NCDs loaded on glassy carbon electrode exhibited high catalytic activity for the CO$_2$ reduction to CO as recording 36 mA/cm$^2$ at $-0.9$ V vs. RHE (90% FE).

The selection of electrolytes is also a critical factor to improve CO$_2$ reduction efficiency. EMIM-BF$_4$ electrolyte was shown to increase selectivity for CO product from CO$_2$ reduction [59]. Salehi-Khojin and coworkers reported that the use of a hybrid electrolyte of choline chloride/KOH was also effective to improve the CO$_2$ reduction selectivity of the MoS$_2$ electrode [67]. Using the choline chloride/KCl buffer instead of EMIM-BF$_4$ afforded 1.5 times higher current density at $-0.25$ V vs. RHE. The high catalytic activity was related to an accumulation of small size K$^+$ ion on the MoS$_2$ surface, which allowed exposure of the MoS$_2$ edge site.

Xie and coworkers devised MoS/Se alloy monolayer to induce poor overlapping of frontier orbitals, which was helpful to enhance the surface activity for the CO$_2$ reduction [68]. The MoS/Se alloy monolayer improved CO production efficiency with 45% FE at $-1.15$ V vs. RHE compared to MoS$_2$ (17%) and MoSe$_2$ (31%) monolayer. On the other hand, in the report by Han and coworkers, the replacement of the chalcogenide with phosphide gave different CO$_2$ reduction products. MoP nanoparticle as supported by In-doped porous carbon (In-PC) converted CO$_2$ to formic acid as recording 43.8 mA/cm$^2$ at $-2.2$ V vs. Ag/AgNO$_3$ with 97% FE [69].

In a rare example, a Mo-cluster has shown promising photocatalytic CO$_2$ reduction ability under visible light illumination. Hexanuclear [Mo$_6$Br$_{14}$]$_2^{-}$ clusters [70] immobilized on graphene oxide [71] showed photocatalytic CO$_2$ reduction to methanol. High nuclearity transition metal cluster of [Mo$_6$X$_1$$\text{L}^8$]$^{2-}$ ($\text{X}^1$ = inner, L$^a$ = apical) enabled visible light activities due to delocalized valence electrons overall metal centers [72,73]. The catalytic CO$_2$ reduction activities of the Mo-based electrocatalysts are compared in Table 1.

### Table 1. Compared CO$_2$ reduction catalytic efficiencies of Mo-based electrocatalysts.

| Catalyst                        | FE  | Current Density       | CO$_2$ Reduction Product (Major) | Ref. |
|---------------------------------|-----|-----------------------|----------------------------------|------|
| Mo electrode                    | 50% | -                     | Methanol                         | [58] |
| layer-stacked MoS$_2$          | 98% | $-65$ mA/cm$^2$ at $-0.76$ V vs. RHE | CO                               | [59] |
| 5% Nb-doped VA-MoS$_2$         | 82% | $-237$ mA/cm$^2$ at $-0.8$ V vs. RHE | CO                               | [60] |
| Ta-doped VA-MoS$_2$            |     | $-98-68$ mA/cm$^2$ at $-0.8$ V vs. RHE | CO                               | [60] |
| MoBiS$_x$ nanosheets           | 71% | $-12.1$ mA/cm$^2$ at $-0.7$ V vs. SHE | Methanol                         | [62] |
| MoS/Se monolayer               | 45% | $-43$ mA/cm$^2$ at $-1.15$ V vs. RHE | CO                               | [68] |
| Cu-doped MoS$_2$               | 85% | $-17$ mA/cm$^2$ at $-1.7$ V vs. SCE | CO                               | [64] |
| NCMSH                           | 93% | $-34.31$ mA/cm$^2$ at $-0.7$ V vs. RHE | CO                               | [65] |
| MoS$_2$ nanoflake (choline chloride) | 93% | $-315$ mA/cm$^2$ at $-0.8$ V vs. RHE | CO                               | [67] |
| N-MoS$_2$@NCDs                 | 90% | $-36$ mA/cm$^2$ at $-0.9$ V vs. RHE | CO                               | [66] |
| MoP@In-PC                      | 97% | $-43.8$ mA/cm$^2$ at $-2.2$ V vs. Ag/AgNO$_3$ | Formic acid                     | [69] |

### 2.4. FDH-Electrode Biohybrid

Formate dehydrogenase (FDH) is the most efficient electrocatalyst for interconversion between CO$_2$ and formate. There have been research interests in the enzyme activity under electrochemical conditions as adsorbed on an electrode surface, or as free in solution.
FDHs are classified as two types of NADH-dependent and metal (Mo or W)-dependent enzymes (NADH = nicotinamide adenine dinucleotide). The bio-electrochemical set-ups of NADH-dependent *Candida boidinii* (CbFDH) have been reported to show selective CO$_2$ reduction to formate [74–79], where the regeneration efficiency of NADH was critical to improving the catalytic system.

Metal-dependent FDH has been studied as attached to an electrode surface. Hirst and coworkers showed reversible interconversion between CO$_2$ and formate by *Escherichia coli* FDH (EcFDH) as adsorbed on a graphite-epoxy electrode [80]. The reversible redox current for the CO$_2$/formate conversion was observed during the cyclic voltammetry scans, and the formate oxidation became favored at higher pH within 6–8 range. Controlled potential electrolysis at $-0.6$ V vs. SHE produced only formate product with $101.7 \pm 2.0\%$ FE.

Redox-active polymer could enhance electron transfer between FDH and electrode. Milton and coworkers used cobaltocene-functionalized polyallylamine (Cc-PAA) to promote electron transfer between EcFDH and glassy carbon electrodes [81]. The electroenzymatic CO$_2$ reduction was detected at $-0.66$ V vs. SHE close to the Cc/Cc$^+$ redox couple of $-0.576$ V vs. SHE. Bulk electrolysis at $-0.66$ V vs. SHE using 50 mM NaHCO$_3$ as the CO$_2$ source provided formate production with FE $99 \pm 5\%$, but the FE dropped to $65\%$ after continuous electrolysis for 12 h.

Bio-hybrid system gives a synthetic vision to develop electrocatalysts with high selectivity and efficiency, although low current density and limited catalytic sites remain as limitations for scale-up. In addition, a hybrid of molecular catalysts with electrode surface would be an alternative method to obtain well-performing catalysts. Ligand design and synthesis are other difficulties, but the conjugation of coordination complexes by electrode surface can provide chances to modify surface reactivity and efficiency of electrocatalysts.

## 3. Nitrogen Fixation

Nitrogen is an essential element in the metabolism of living organisms and one of the major elements that make up the body. The only way to take atmospheric N$_2$ into organisms is via the nitrogen fixation process [82,83]. In a symbiotic relation, plants feed nitrogen-fixing bacteria with sugars as a reducing equivalent to perform the reduction of N$_2$ to NH$_3$, which is in return absorbed by plants. Although nature performs the process very efficiently, the direct N$_2$ reduction has been one of the challenges in the research area of synthetic catalysts [84]. The industrial Haber–Bosch process takes charge of global ammonia production, but this process occupies 1% of annual fossil fuel consumption and 3% of annual CO$_2$ emission because of the production conditions demanding high pressure and high temperature [85,86]. Mild reaction conditions are highly craved to decrease the consumption of the limited energy resources as well as anthropogenic CO$_2$ emission [87,88]. There exist many research efforts to elucidate the mechanism of the natural catalytic system, nitrogenase, by investigating the structural features and synthetic model complexes [89–91]. In addition, heterogeneous catalysts were developed for nitrogen reductions, and bio-hybrid catalysts were studied in a way of attaching nitrogenase to an electrode surface.

### 3.1. Nitrogenase

In the 1960s, X-ray structure of the FeMo-nitrogenase active site was obtained, and thereafter the structural features and the relation with the enzyme reactivity have been studied to elucidate the nitrogen reduction process [92–94]. The N$_2$ reduction is a series of electrochemical reactions requiring overall $6e^-/6H^+$ input. The FeMo-cofactor facilitates the nitrogen reaction, and the co-existing P cluster is in charge of the electron-transfer steps. The FeMo cluster is buried under the enzyme protein to selectively promote the multi-electron reduction process (Figure 3).

$$\text{N}_2 + 8\text{H}^+ + 16\text{MgATP} + 8\text{e}^- \rightarrow 2\text{NH}_3 + \text{H}_2 + 16\text{MgADP} + 16\text{Pi}$$
 Nitrogen is an essential element in the metabolism of living organisms, being a key component of amino acids, proteins, and nucleic acids. The fixation of atmospheric nitrogen (N\(_2\)) into forms usable by living systems is a complex process that occurs through both biological and industrial means.

The FeMo-cofactor has a double-cubane type of Mo\(_7\)Fe\(_7\)S cluster, where each cubane is bonded by a carbide (C\(^{-}\)) center and a Mo atom is positioned at an end of the cluster [95–97]. Although the reaction mechanism remains obscure in the research of N\(_2\) reduction catalysts, both the Fe and Mo sites have been considered as the active sites for the nitrogen reactions. In the current review, we focus on the Mo-based model complexes.

3.2. Structural Analogs of Nitrogenase

In 1978, Holm and coworkers synthesized [Mo\(_2\)Fe\(_6\)S\(_8\)] (22) cluster as a model of the FeMo-nitrogenase through a self-assembly method [98,99]. Later, in 1982, the same group reported a cubane-type structure of [MoFe\(_2\)S\(_4\)] (23) by removing a Mo ion from [Mo\(_2\)Fe\(_6\)S\(_8\)], [100,101] which showed very similar EXAFS data as the original FeMo-cofactor [102]. In 1993, Coucouvanis and coworkers synthesized a citrate-stabilized [MoFe\(_2\)S\(_4\)] (24), similar to the homocitrate-coordinated FeMo-nitrogenase [103]. In addition, [(Tp)MoFe\(_3\)S\(_4\)Cl\(_3\)]\(^{-}\) (25) cluster was synthesized using hydrotrispyrazolylborate(Tp) ligand as a model of homocitrate [104]. Along with the structural modeling of the FeMo-cofactor, Mo-based complexes were studied for the catalytic N\(_2\) reduction [105–107] (Scheme 12).

![Scheme 12. Nitrogenase model complexes.](image)

3.3. Synthetic Electrocatalysts for N\(_2\) Reduction

3.3.1. Homogeneous Mo Complexes for N\(_2\) Reduction

In 1988, Hidai reported examples of converting N\(_2\) to silylamines using zero-valent Mo coordinated by phosphine ligands, cis-Mo(N\(_2\))\(_2\)(PMe\(_3\)Ph)\(_4\) (26) and Mo(N\(_2\))\(_2\)(dpe)\(_2\) (27) (Scheme 13) [108]. Complex 26 produced 23.7% N(SiMe\(_3\))\(_3\) under optimized conditions of N\(_2\) using Me\(_3\)SiCl and Na (or Li) as reductant, whereas complex 27 showed less activity of 9.7% conversion yield under the same condition. The monodentate phosphine made a more active Mo site than the bidentate phosphine. Even though the conversion yield was low, it gave early examples of Mo-phosphine catalysts for N\(_2\) conversion reactions.
In 2003, Yandulov and Schrock used a high-valent Mo(III-IV) ion stabilized by a tetradeptate triamidoamine ligand for the reduction of N₂ to NH₃ [109]. The coordination of a hexaisopropylferrocenyltriphenylamine (HIPT) ligand to Mo(IV) ion gave [HIPT(N₂)MoCl] where the six hexaisopropylferrocenyl groups sterically enclosed the Mo active site [110]. The bulky ligand system prevented dimerization of the complex by conserving the single Mo center [106,111]. Unlike the FeMo-cofactor, the Mo complex was coordinated by organic N donors, but the reactivity study of [HIPTN₃N]Mo³⁺(N₂) (28) species provided implemental results to understand an N₂ reduction process (Scheme 13). Using a proton source of [(2,6-lutidinium)(BARF)] and decamethyl chromocene as a reductant, complex 28 generated 7.56 equiv. of NH₃ per a Mo ion and 63% yield per a reductant, which was comparable to that of FeMo-nitrogenase (75% NH₃, 25% H₂) [112]. They proposed an N₂ reduction mechanism catalyzed by a single Mo site based on spectral data and X-ray crystal structures of intermediates. X-ray crystal structures and spectral data characterized the nitrogen reaction intermediates such as Mo(N₂), Mo=N=NH₂, Mo≡N, [Mo=N-NH₃]⁺, [Mo=NH]⁺, [Mo-NH₃]⁺, and MoNH₃, which suggested the N₂ reduction pathway including 6e⁻/6H⁺ processes [113–117]. In the proposed pathway, protons bind to one nitrogen to release the first NH₃, and the next protonation occurs on the remaining nitrogen to produce the second NH₃ (Scheme 14). Their studies gave a research basis for a Mo-based N₂ reduction process [118].

Scheme 13. Homogeneous Mo complexes.

Scheme 14. N₂ reduction pathways by Schrock complex.
In 2011, Nishibayashi and coworkers tried to improve the \( \text{N}_2 \) reduction activity of Mo complexes by utilizing redox-active ligands. They modified the Hidai complex (26) with ferrocenyl diphenosilane ligand to prepare trans-Mo(N\(_2\))\(_2\)(phenyl)\(_2\) (29) (defp = diethylphosphinoferrocene) [119]. Complex 29 performed the silylamine production under 1 atm of \( \text{N}_2 \) at room temperature using Na and Me\(_3\)SiCl. Me\(_3\)SiCl formed Me\(_3\)Si\(^+\) radical in the presence of Na reductant, and a Me\(_3\)Si\(^+\) radical derived the \( \text{N}_2 \) reaction to produce N(SiMe\(_3\))\(_3\) (226 equiv. per a Mo atom for 200 h). Acid post-treatment of the produced silylamine afforded \( \text{NH}_3 \). The same group used other redox-active PNP type ligands for Mo catalysts [120]. Reduction of the \([\text{MoCl}_3(\text{PNP})]\) species with Na/Hg under \( \text{N}_2 \) formed an \( \text{N}_2 \)-bridged di-Mo complex \([\text{Mo}(\text{N}_2)\text{H}_2(\text{PNP})]_2(\mu-\text{N}_2)\) (30a-c) (Scheme 13). Subsequent reaction with 4 equiv. of HBF\(_4\)-OEt\(_2\) and pyridine generated a Mo-hydrazide species, and further reaction with \([\text{LuTH}]\text{OTf}\) produced \( \text{NH}_3 \) (23.2 equiv. of \( \text{NH}_3 \) per a catalyst). The reaction mechanism was explained similarly as proposed by Schrock, where one nitrogen site receives \( 3e^- / 3\text{H}^+ \) to release \( \text{NH}_3 \) and subsequent \( 3e^- / 3\text{H}^+ \) reaction of the remaining Mo(N) generates (Scheme 15). In the screening of reductants of Cr-Cp (\( E_{1/2} = -0.88 \text{ V vs. } \text{Ag/Ag}^+ \) in MeCN), Co-Cp (\( E_{1/2} = -1.15 \text{ V} \)), Cr-Cp\(^*\) (\( E_{1/2} = -1.35 \text{ V} \)) and proton sources such as \([\text{LuTH}]\text{OTf}\) (pKa 14.4 in MeCN), pyridinium trifluoromethanesulfonate (pKa 12.6), and HOTF (pKa 2.6), the Nishibayashi complex exhibited the \( \text{N}_2 \) reduction activity with Co-Cp and Cr-Cp\(^*\), but not with Cr-Cp [121]. The complex showed the best performance with the combinatory use of Co-Cp and \([\text{LuTH}]\text{OTf}\).

The electronic property of the pyridine ligand affected the catalytic reaction rate by modulating Mo–N≡N–Mo bond strength [122]. In comparison with the \( v(\text{NN}) \) frequency (1944 cm\(^{-1}\)) of unmodified pyridine (30a), the para-substitution with a phenyl group increased the frequency to 1950 cm\(^{-1}\) (30b), whereas the methoxy group decreased to 1932 cm\(^{-1}\) (30c). The relative bond strength was reflected in the \( \text{N}_2 \) reduction reactivity of catalysts. Complex 30a provided 21–23 equiv. of \( \text{NH}_3 \) production, but 30c with the electron-donating methoxy substituent induced the highly efficient \( \text{NH}_3 \) formation (34 equiv. per catalyst) by accelerating the protonation step. Similar to the P cluster of the nitrogenase, the substitution of a redox-active ferrocene assisted the catalytic reaction (30d–g) [123]. Ferrocene-attached Mo complexes showed a similar \( v(\text{NN}) \) stretching frequency as the complex 30a but increased the \( \text{NH}_3 \) production to 37 equiv. per catalyst. Although unmodified ferrocene did not affect the NN bond strength, modification of the ferrocene with ethyl or phenyl groups caused the slight shift of the \( v(\text{NN}) \) value indicating electronic connectivity through the chemical bonds. The \( v(\text{NN}) \) value was measured as 1939 cm\(^{-1}\) with the ethyl-ferrocene and 1951 cm\(^{-1}\) with the phenyl-ferrocene. Consistent with the

![Scheme 15. \( \text{N}_2 \) reduction pathway by Nishibayashi complex.](image-url)
electron-donating effect, the ethyl-ferrocene resulted in 30 equiv. of NH₃ formation per catalyst, which was higher than 10 equiv. of NH₃ of the phenyl-ferrocene.

The Nishibayashi type PNP-Mo catalysts began the N₂ reduction in the N₂-bound Mo state after a halide abstraction step. They recently reported the presence of iodide ligand rather improved the catalytic activity because of the electron-withdrawing property. PNP-MoL₃ complexes (31a–d) were synthesized with phosphine ligands varied by different substituents such as isopropyl, tert-butyl, adamantyl, and phenyl groups (Scheme 16) [124]. The P(tert-butyl)₂ group gave the highest NH₃ production. The catalytic activity was further examined by changing the para-position of pyridine with MeO, Me, Ph, Fc, and Rc (32a–e) with keeping the P(tert-butyl)₂ moiety of PNP ligand. At the time, the para-Ph substituent showed the highest activity of 90 equiv. of NH₃ production, which was much higher than the case of para-MeO substituent [125]. The trend was opposite from the case of N₂-bridged dinuclear Mo complexes. Complex 31b exhibited a maximum 415 equiv. of NH₃ production per catalyst, which was 35 times higher activity than the N₂-bridged Mo₂ complex. Furthermore, they examined the effect of PNP-type carbene ligands of 1,3-bis((di-tert-butylphosphino)methyl)benzimidazol-2-ylidene (PCP-1), 1,3-bis(2-(di-tert-butylphosphino)ethyl)imidazol-2-ylidene (PCP-2) [126] (Scheme 16). The PCP-1-Mo (33) produced 100 equiv. of NH₃ per catalyst, but the PCP-2-Mo (34) showed a low reactivity of 1.6 equiv. of NH₃ per catalyst. The identity of the reducing agent and proton source also affected the nitrogen reduction activity of Mo catalysts. Complex 33 showed the high activity when used together with SmI₂ and H₂O (or ethylene glycol) instead of CoCp* and [LutH]OTf. The combinatory use of SmI₂ and ethylene glycol resulted in turnover frequency (TOF) of 7000 h⁻¹ for the NH₃ generation, and the condition using H₂O as a proton source slightly decreased TOF to 6800 h⁻¹ [127]. Using ethylene glycol as a proton source produced 22% (relative to a reductant) of H₂ as a side product, but H₂O reduced the ratio to ~2%. The optimized condition using H₂O and SmI₂ increased the NH₃ productivity of complex 33 to 4350 equiv. per catalyst and TOF to 112.9 min⁻¹, which was close to the nitrogenase activity of 40–120 min⁻¹ [128].

Scheme 16. Homogeneous PNP-Mo complexes.

3.3.2. Heterogeneous Mo-Containing N₂-Reduction Electrocatalysts

Nitrogen reduction catalysts should deliver protons selectively to a bound nitrogen on their active sites, because the thermodynamic potential of a competitive proton reduction is relatively low. For this, the intrinsic property of an active metal center is an important factor to determine the N₂ reduction reactivity of catalysts. Novel transition metals have shown nitrogen reactivities, but their limited reserves and high-cost issues are obstacles for their industrial scale-up as catalysts [129–135]. Earth-abundant metals are promising alternatives for nitrogen catalysts. Mo ions as the forms of MoS₂, MoO₃, MoN, Mo₂N, and Mo₂C were proven to be active for the N₂ reduction. The specific affinity of Mo ion to nitrogen has been.
reported in the previous experiments [136,137]. In addition, the utilization of mixed metal elements could increase N\textsubscript{2} reactivity and promote electron-transfer by tuning surface energy states.

The N\textsubscript{2} reactivity seems to be varied by Mo crystal orientation. Wang and coworkers reported that Mo(110) plane has higher reactivity with N\textsubscript{2} than other planes of (200) and (211) [138]. They prepared four types of Mo electrodes of Mo-foil, Mo-A-R, Mo-D-R-1h, and Mo-D-R-5h through electrodeposition, and Mo-D-R-5h showed the highest (110) orientation ratio based on XRD patterns [139–141].

Outermost Mo is an active site, but the reactivity and mechanism are determined by supporting elements. Sun and coworkers studied different reactivities of Mo, conjugated by O, S, and N atoms, by comparing MoO\textsubscript{3}, MoS\textsubscript{2}, and MoN [142–144]. Edge sites of Mo chalcogenides are known to be active for N\textsubscript{2} reaction. MoN surface has shown ~0.2 lower overpotential than Mo chalcogenides. It is possibly understood that as a surface Mo-N is reduced to NH\textsubscript{3}, an empty Mo site facilitates subsequent N\textsubscript{2} adsorption and reduction process.

Conductive support was also an important component to improve the electrocatalytic performance of MoS\textsubscript{2}, because the large conductive surface area supports more MoS\textsubscript{2} active area as well as increases surficial electrical conductivity. Tian and coworkers achieved significant improvement of FE (10.94% at −0.3 V vs. RHE) of MoS\textsubscript{2} using Ti\textsubscript{3}C\textsubscript{2} MXene [145].

The catalytic efficiencies and reaction rates of the Mo-based electrocatalysts are compared in Table 2.

| Catalyst                  | FE      | NH\textsubscript{3} Formation Rate | Ref.   |
|---------------------------|---------|-------------------------------------|--------|
| (110)-oriented Mo nanofilm | 0.72%   | 3.09 × 10\textsuperscript{-11} mols\textsuperscript{-1} cm\textsuperscript{-2} at −0.49 V vs. RHE | [138]  |
| MoO\textsubscript{3} nanosheets | 1.9%    | 4.80 × 10\textsuperscript{-10} mols\textsuperscript{-1} cm\textsuperscript{-2} at −0.5 V vs. RHE | [142]  |
| MoN nanosheets            | 1.15%   | 3.01 × 10\textsuperscript{-10} mols\textsuperscript{-1} cm\textsuperscript{-2} at −0.3 V vs. RHE | [143]  |
| MoS\textsubscript{2}      | 1.17%   | 8.08 × 10\textsuperscript{-11} mols\textsuperscript{-1} cm\textsuperscript{-2} at −0.5 V vs. RHE | [144]  |
| 1T-MoS\textsubscript{2}@Ti\textsubscript{3}C\textsubscript{2} | 10.94%  | 30.33 µg h\textsuperscript{-1} mg\textsuperscript{-1} cat. at −0.3 V vs. RHE | [145]  |

### 3.4. Nitrogenase-Electrode Biohybrid

In general, synthetic modeling studies focus on enzyme active sites, but protein structure should be an important factor to control the enzyme reaction. Even a small mutation of a nearby amino acid could distort the entire enzyme reactivity. For example, the substitution of a nearby β-98\textsuperscript{Ty} Tyr amino acid to β-98\textsuperscript{His} His deactivated the N\textsubscript{2} reduction ability of the mutated FeMo-nitrogenase [146]. However, a reduction of hydrazine (N\textsubscript{2}H\textsubscript{2}) to NH\textsubscript{3} still occurred in the mutated FeMo-nitrogenase. Interestingly, the mutation by β-98\textsuperscript{His} improved electron-accepting ability from an un-natural reducing agent to promote reductions of azide (N\textsubscript{3}−) or nitrite (NO\textsubscript{2}−) to NH\textsubscript{3} [147]. Using electron mediators such as polyaminocarboxylate-ligated Eu [126] and polyallylamine (PAA) polymer-CoCp\textsubscript{2} [148] further improved reduction efficiencies. Rather in the presence of Fe-protein, without using an additional electron mediator, electron transfer between Fe-protein and FeMo-cluster became slow. Badalyan and coworkers showed experimentally that electron transfer between FeMo-cluster and Fe protein is the rate-determining step by calculating reaction rate constants using cyclic voltammetry data [149].

King and coworkers made a biohybrid system by attaching FeMo-nitrogenase to CdS nanorods for applications to a photocatalytic reduction of N\textsubscript{2} to NH\textsubscript{3} [128]. In the biological reaction, electron transfer steps from the P cluster to the FeMo-cluster require 16ATP (\(E_{m} = −0.42\) V) (ATP = adenosine triphosphate). In the bio-hybrid system, irradiation of CdS nanorod with 405 nm wavelength generated excited electrons with −0.8 eV, which was transferred to the FeMo-nitrogenase to proceed with the N\textsubscript{2} reduction reaction. The TOF was 75 min\textsuperscript{-1} and the NH\textsubscript{3} production rate was 315 ± 55 nmol(mg MoFe protein\textsuperscript{-1}) min\textsuperscript{-1}. 

which was 63% less activity compared to the enzyme activity with the presence of Fe protein and ATP. Upon using nitrogenase inhibitors such as acetylene, CO, and H$_2$ [150–152], the enzyme activity became silent excluding a possible N$_2$ reduction by CdS only.

Biohybrid of FeMo-nitrogenase with electrode enabled the enzyme to function in the absence of ATP, and thereby provided ways to study the enzyme reaction out of intracellular conditions. In future research, new biohybrid designs are required to decrease overpotential for the N$_2$ reduction as well as to develop methodologies for the transformation of N$_2$ to useful molecules.

4. H$_2$ Evolution

The proton reduction is always a competitive reaction in the electrocatalytic reductions of CO$_2$ and N$_2$, because the 2H$^+$/H$_2$ reduction is thermodynamically favored. However, on the other hand, hydrogen molecules can be used as the simplest energy carrier for solar or electric energy conversion and storage [153]. Due to the importance, various transition metal-based electrocatalysts were developed for H$_2$ evolution [154–156].

4.1. Homogeneous Mo Complexes for H$_2$ Evolution

Nature does not use Mo metal for metabolic hydrogen reactions of H$_2$ evolution and splitting, but hydrogenase active site inspired ligand design for Mo complexes. It was shown that anionic cyclopentadienyl (Cp) ligand has a similar electronic property as the Ni ligation sphere of the [NiFe]-hydrogenase active site [157]. Felton and Donovan reported that [(η$^5$-C$_5$H$_5$)Mo(CO)$_2$(dppe)Br (35)] complex promoted the reduction of acetic acid in acetonitrile with 0.9 V overpotential [158]. Fan and Hu utilized poly-hapto ligands to prepare Mo-carbonyl complexes of (η$^5$-C$_5$H$_5$)Mo(CO)$_2$(dppe)Br (36), (η$^5$-C$_5$H$_5$)Mo(CO)$_2$(dppe)Br (37), (η$^5$-C$_5$H$_5$)Mo(CO)$_2$I (38), and (η$^5$-C$_5$H$_5$)Mo(CO)$_2$PPh$_3$I (39) (Scheme 17) [159]. Complex 36–39 showed similar reactivities of the halide dissociation during the cyclic voltammetry in MeCN solution and also exhibited similar catalytic activity of 16–27 TON for 5 h for the reduction of trifluoroacetic acid as requiring ~1 V overpotentials.

Scheme 17. Homogeneous Mo complexes for H$_2$ evolution.

Hydrodesulfurization utilizes Mo-sulfides as a catalytic surface [160]. Similar to the MoS$_2$ active site, Mo-sulfide moiety has been synthesized in the Mo coordination environment. DuBois and coworkers used Cp ligand to obtain a sulfide bridged dinuclear Mo complex, [(η$^5$-C$_5$H$_5$)Mo(µ-S$_2$CH$_2$)]$_2$ (Scheme 17) (40). Complex 40 facilitated reduction of p-cyanoanilinium tetrafluoroborate at −0.7 V vs. Fe$^+/}$/F in MeCN solution containing 0.3 M of Et$_4$NBF$_4$ electrolyte [161]. Controlled-potential electrolysis at −0.96 V vs. Fe$^+}$/F generated 10.6 mol of H$_2$ gas per catalyst with 98 ± 5% FE. The catalytic activity was compared using different proton sources such as triflic acid (pKa = 2.6 in MeCN), p-cyanoanilinium tetrafluoroborate (7.6) and p-cyanoanilinium tetrafluoroborate (9.6). Higher pKa of the proton source shifted the proton reduction potential to the negative
direction. Kinetic studies suggested that the elimination of H2 from the catalytic site is the rate-determining step.

Chang and coworkers synthesized the Mo(S2) moiety in a pentadentate polypyridyl Mo complex [(k^5-PY5Me)MoS2]^2+ (42) (PY5Me = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine) from a reaction of [(k^5-PY5Me)Mo(k^1-CF3SO3)](CF3SO3) (41) with S8 (Scheme 18) [162]. Complex 42 generated H2 in acetate buffer (pH 3) at the onset potential of −0.58 V vs. SHE. Controlled potential electrolysis at −0.83 V overpotential produced H2 gas with ~100% FE and 280 mol/s TOF. Albeit less active than 42, Complex 41 also showed catalytic activity to produce H2 gas in 0.6 M phosphate buffer (pH 7) requiring 0.52 V overpotential. Controlled potential electrolysis at 0.64 V overpotential produced H2 gas as 1600 mol/h TOF per catalyst. Complex 41 also produced H2 gas in seawater at the onset potential of −0.81 V vs. SHE with 1200 mol/h TOF at −1.40 V vs. SHE. [163].

Scheme 18. Structure of homogeneous Mo complexes for H2 evolution.

Streb and coworkers observed that partial substitution of terminal disulfide in [Mo3S13]^2− by H2O to [Mo3S7(H2O)x]^2−−x− increased the catalytic activity. Instead, the substitution of terminal disulfide with halides to [Mo3S7−X]^2− (X = Cl, Br) decreased significantly the HER activity [164]. They suggested that, if terminal disulfide is protonated, energetically stable and catalytically inactive species are formed. It looks critical the formation of a vacant coordination site on a terminal Mo to generate catalytically active Mo-H.

Eisenberg and coworkers used dithiolene ligands to obtain Mo-sulfides moiety in MoL2(bdt)2 (43a–g) (bdt = benzene-1,2-dithiol) (Scheme 19) [11]. Two-electron reduction of complexes 43a–e in MeCN/H2O (9:1) solution dissociated isonitrile ligands to generate Mo(bdt)2, which was the active species for the catalytic HER. Complexes 43a–g also showed photochemical HER in MeCN/H2O solution under the conditions of using [Ru(bpy)3]Cl2 as a photosensitizer, 0.2 M ascorbic acid (pH 4) as an electron donor. Complexes 43a gave the highest TON of 520 for 24 h than other complexes (<475 TON).

Scheme 19. Structure of homogeneous Mo complexes for H2 evolution.

Moly-oxo complexes have shown interesting proton reduction activities. Zhan and coworkers synthesized cis di-oxo Mo complex, [MoIV(L)(O2)] (Scheme 20) (44) (L = 2-pyrididlamino-N,N-bis(2-methylene-4-methoxy-6-tertbutylphenol)) [165]. Complex 44 promoted proton reduction at 0.25 M phosphate buffer (pH 7) recording 360 mol/h TOF (907 mV overpotential). Next, fluorine-substitution of [MoL'(O2)] (Scheme 20) (45) (L' = 2-pyrididlamino-N,N-bis(2-methylene-4,6-difluorophenol)) gave higher TOF of 756 mol/h
(89% FE) at $-1.61$ V vs. Ag/AgCl in mixed acetonitrile/water (2:3) solution containing phosphate buffer (pH 6) [166].

Kim and coworkers reported the proton reactivity of $[\text{MoO(S}_2\text{C}_2\text{Ph}_2]_2]^{-2}$ (46) in MeCN solution. Treatment of protons ($\pi$-toluenesulfonic acid) with complex 46 in MeCN processed dehydration of the complex to give $[\text{Mo(MeCN)}_2(S_2\text{C}_2\text{Ph}_2)_2]$ (47) (Scheme 21) [167]. Complex 47 had poor solubility in polar solvents, and the fast dehydration of 46 prevented the use as an electrocatalyst. However, modification of the dithiolene ligand could make Mo ion function as HER electrocatalyst. Fontecave and coworkers utilized quinoxaline–pyran-fused dithiolene (qpdt$^{2-}$), analogous to the molybdopterin (MPT), to prepare $(\text{Bu}_4\text{N})_2[\text{MoO(qpdt)}_2]$ (48) (Scheme 22) [168]. The qpdt$^{2-}$ ligand assisted the Mo-oxo site to catalyze HER. Electrocatalytic proton reduction of trifluoroacetic acid was detected at $-0.55$ V vs. Ag/AgCl, and TOF of 1030 s$^{-1}$ was obtained at $-1.3$ V vs. Ag/AgCl (FE 86% for 3 h). Complex 48 also facilitated photocatalytic HER with $[\text{Ru(bpy)}_3]^{2+}$ in 0.1 M ascorbic acid (pH 4) as recording TON 500 for 15 h.

4.2. Heterogeneous Mo-Containing H$_2$ Evolution Electro catalyst

In 2005, Norskov and coworkers calculated the free energy of atomic hydrogen bonding ($\Delta G^0_{\text{H}}$) to MoS$_2$ surface and compared it with other catalysts such as enzymes (FeMo cofactor and NiFe hydrogenase) and metal surfaces of Au, Pt, Ni, and Mo [169]. Density functional theory (DFT) calculation results suggest that Ni and Mo bind strongly to atomic hydrogen; however, since the next proton/electron transfer steps are thermodynamically uphill, the H$_2$-releasing step becomes slow as making those metals not suitable for HER. Interestingly, the metalloenzymes of FeMo-nitrogenase and NiFe-hydrogenase using Ni and Mo elements had similar hydrogen-binding energy ($\Delta G^0_{\text{H}} \sim 0$) as Pt. Plane MoS$_2$ was inactive for HER, but the edge of MoS$_2$ had a bit positive $\Delta G^0_{\text{H}} \sim 0.1$ eV in a suitable range for HER. Graphite-supported MoS$_2$ with enlarged edge area showed electrocatalytic HER with 0.1–0.2 V overpotential.
Chorkendorff and coworkers could modify the MoS$_2$ edge area by varying sintering temperature (Figure 4a) [170]. The MoS$_2$ prepared from 400 °C sintering had a longer edge length than another case of 550 °C sintering, and accordingly showed a higher HER current density of $3.1 \times 10^{-7}$ A/cm$^2$ compared to $1.3 \times 10^{-7}$ A/cm$^2$ of the latter. Albeit lower than the Pt electrode, the MoS$_2$ edge exhibited higher current density than other common metal elements. They also showed photocatalytic HER activity of mixed MoS$_2$ surface as deposited on Ti/n$^+$/p-Si photocathode [171]. The MoS$_2$ was electrodeposited on Ti-protected n$^+$/p-Si electrode by cyclic voltammetry (CV) scans at 0.137–1.247 V vs. RHE. The MoS$_2$ | Ti/n$^+$/p-Si photocathode showed HER activity above 0.33 V vs. RHE under the illumination of red light.

The electrodeposition method seems to be not suitable to produce a large number of catalysts, and unstable species may not persist during cyclic voltammetry scans. Hu and coworkers reported that unsaturated MoS$_2$ provides a more active site for HER [172]. They prepared MoS$_2$ film by electro-polymerization method (Figure 4b), which exhibited higher catalytic activity than another case of 550 °C sintered single crystal and MoS$_2$ nanoparticles. They explained that is because amorphous MoS$_2$ increases sulfur defects at the surface [173]. The same group investigated the effects of growth mechanism and catalyst mass, but they reported that the catalyst mass dominantly affected the catalytic efficiency (Figure 4c) [174].

Mo sulfur clusters have shown similar active sites as MoS$_2$. Chorkendorff and coworkers adsorbed cubane type [Mo$_5$S$_4$]$^{4+}$ cluster to highly oriented pyrolytic graphite [175]. [Mo$_3$S$_4$]$^{13+}$ cluster showed similar overpotential as MoS$_2$ nanoparticle. Even higher TOF of 0.07 s$^{-1}$ was measured than 0.02 s$^{-1}$ of MoS$_2$ nanoparticle, but it was unstable during successive potential scanning.

Bensenbacher and coworkers synthesized [Mo$_3$S$_{13}$]$^{2-}$ nanocluster by a wet chemical method of (NH$_4$)$_6$Mo$_7$O$_{24}$ and ammonium polysulfide [176]. [Mo$_3$S$_{13}$]$^{2-}$ showed HER activity at 0.1 V onset potential and 0.18 V overpotential at 10 mA/cm$^2$ (TOF 3 s$^{-1}$). Li and coworkers synthesized Mo$_3$S$_{13}$ film by electrodeposition, which showed a higher catalytic rate and lower overpotential by ~40 mV than Mo$_3$S$_{13}$ film prepared by drop-casting of (NH$_4$)$_2$Mo$_3$S$_{13}$+2H$_2$O [177]. The increased electrical conductivity enhanced catalytic efficiency. Xu and coworkers improved HER efficiency by attaching [Mo$_3$S$_{13}$]$^{2-}$ to highly conductive reduced graphene oxide-carbon nanotube (rGO-CNTs) aerogels, which recorded a lower overpotential by 74 mV than pure [Mo$_3$S$_{13}$]$^{2-}$ [178]. Wu and coworkers reported that dimeric [Mo$_3$S$_{12}$]$^{2-}$ cluster slightly improved the HER activity by recording 0.16 V overpotential at 10 mA/cm$^2$ (TOF ~3 s$^{-1}$) compared to [Mo$_3$S$_{13}$]$^{2-}$ [179]. They reported hydrogen adsorption free energy $\Delta G_{\text{ads}}$(H) of [Mo$_3$S$_{12}$]$^{2-}$ (~0.05 eV) is closer to zero than other surfaces such as [Mo$_3$S$_{13}$]$^{2-}$ (~0.08 eV), MoS$_2$ (0.08 eV), and Pt(111) (~0.09 eV).

Min and coworkers reported HER activity of [Mo$_3$S$_{13}$]$^{2-}$ using [Ru(bpy)$_3$]Cl$_2$ and ascorbic acid under visible light (≥420 nm). Initial TOF of 335 h$^{-1}$ was measured, but it had a problem of gradual decomposition [180]. The photocatalytic stability of [Mo$_3$S$_{13}$]$^{2-}$ was improved by Zang and coworkers [181]. They encapsulated [Mo$_3$S$_{13}$]$^{2-}$ in ethidium bromide covalent organic frameworks (EB-COFs). The COF-encapsulation did not decrease significantly the catalytic activity relative to a free [Mo$_3$S$_{13}$]$^{2-}$ cluster. Mo$_3$S$_{13}$@EB-COF maintained photocatalytic HER for 8 h by recording 21,465 μmol g$^{-1}$ h$^{-1}$ rate, furthermore which showed the stable catalytic performance during the recycling test of 4 times of 5 h experiment.

Artero and coworkers studied the structure and reaction mechanism of amorphous MoS$_2$ (α-MoS$_2$), which had polymer-based on [Mo$_3$S$_{13}$]$^{2-}$ cluster sharing disulfide ligand [182]. They suggested that the reaction of terminal disulfide with proton and electron releases HS$^{-}$ to generate unsaturated Mo$^{3+}$ active site.

Octahedral molybdenium clusters are red near-IR phosphorescent emitters and showed high photocatalytic HER activity. Feliz and coworkers studied the catalytic performance of the (TBA)$_2$[Mo$_8$Br$_{14}$F$_{56}$] (TBA = tetra-n-butylammonium) cluster in aqueous solution in the presence of triethylamine (TEA) [183]. The catalytic activity of the [Mo$_8$Br$_{14}$]$^{4+}$-
cluster unit was enhanced by the in situ generation of the [Mo8Br24F18(OH)4]2− and [Mo8Br24F18(OH)4]2− and [Mo8Br24(OH)4]2− species. In the same work, the cluster unit was coordinatively immobilized onto graphene oxide (GO) surfaces. The resulting material, (TBA)2Mo8Br8@GO, enhanced the cluster stability in a water/Methanol mixture and under photoradiation. Its catalytic performance was superior to that of GO, it decreased with respect to that of the molecular cluster complex. The TOF values with respect to atomic molybdenum were 5 × 10−6 s−1 and 3 × 10−4 s−1 for the heterogeneous and the homogeneous materials, respectively. Recently, the (TBA)2[Mo8I8(O2CCH3)4]2+ was also coordinatively immobilized onto GO to give (TBA)2Mo8I8@GO [184]. To assure the cluster stability of the cluster units under photocatalytic conditions, both materials were tested in vapor water photoreduction. Even after longer radiation exposure times, the catalysts remained stable and recyclability of both catalysts was demonstrated. The TOF of (TBA)2Mo8I8@GO is three times higher than that of the microcrystalline (TBA)2[Mo8I8(O2CCH3)4]2+, in agreement with the better accessibility of catalytic cluster sites for water molecules in the gas phase. In the framework of the study of the photocatalytic properties of the [Mo8I8]4+ cluster units, one of the most emissive octahedral metal clusters, [Mo8I8(OCCOCF3)4]2−, was immobilized onto graphene sheets through pyrene-containing organic cations as supramolecular linkers [185]. These non-covalent interactions enhanced the photocatalytic activity of the nanocomposite by 280% with respect to the molecular cluster and graphene counterparts. The improvement of the H2 production activity is attributed to the synergetic effect between graphene and the hybrid cluster complex because graphene facilitates the charge-separation activity and enhances electron transfer of the cluster photocatalyst.

Lana-Villarreal and coworkers reported photocatalytic HER activity of Mo2S3 cluster as immobilized on TiO2 surface [186]. Functionalized bipyridyl ligand of Mo2S3Br4(diimino) cluster enabled adsorption of the cluster on TiO2 surface. The immobilized Mo2S3 cluster decreased the HER overpotential by 0.3 V as recording 1.4 s−1 TOF. Despite the moderate catalytic activity, it gave an example to immobilize molecular cluster on electrode surface. Fabrication of hetero-metal chalcogenides was an effective method to improve catalytic activities of Mo-based electrode materials. Doping of metal promotors possibly improves the intrinsic activity of unsaturated Mo sites. The electrocatalytic effect of Cu/Mo heterometals was examined by Tran and coworkers [187]. Cu2MoS4 was synthesized by the solvothermal reaction of [Cu(CH3CN)][BF4] and (NH4)2[MoS4], and the obtained Cu2MoS4 crystals were stable under air for weeks.

Both MoS2 and CoSe2 were active for HER, and the synergistic effect of combined MoS2 and CoSe2 was examined by Gao and coworkers [188]. MoS2/CoSe2 showed the HER activity close to commercial Pt/C. Interaction of the first-row transition metal Co with S could form S2− and S2− states, which possibly assisted MoS2 growth. MoSe2 was relatively less studied compared to MoS2. Since the atomic hydrogen adsorption energy was measured to be lower with MoSe2 than that of MoS2, MoSe2 also showed an efficient HER activity [189]. Sasaki and coworkers improved corrosion stability of Ni/Mo-alloy by NiMoOx nanosheet, where metal stabilizing effect of nitride possibly improved the stability [190]. Mo phosphide (MoP) is a known hydrodesulfurization catalyst. Jaramillo and coworkers compared catalytic HER activity of crystalline MoP and molybdenum phosphosulfide (MoP/S) [191]. Both the MoP and MoP/S were active for HER, but MoP/S showed the higher electrocatalytic activity than MoP.

Electrocatalytic HER activities of commercial MoB and Mo2C have been reported [192]. Two electrode materials showed similar catalytic activity and were usable under both acidic and basic conditions, exhibiting similar activity and durability in continuous electrolysis for 48 h.

Leonard and coworkers reported the synthesis of various Mo-carbide materials such as α-MoC1−x, β-Mo2C, η-MoC, and γ-MoC with different stacking sequences, and compared their HER activities [193]. The β-Mo2C, η-MoC, and γ-MoC had similar hexagonal crystal structure, but the stacking sequence of β-Mo2C was ABAB, η-MoC was ABCABC, and γ-MoC was AAAA packing. α-MoC1−x had a cubic structure as ABCABC stacking sequence.
The β-Mo$_2$C showed the highest HER activity, and the catalytic activities of the others were obtained in the order of: γ-MoC > η-MoC > α-MoC$_{1-x}$. The γ-MoC showed stable catalytic activity with −1.95 mA/cm$^2$ at −340 mV vs. RHE in the continuous electrolysis for 18 h.

Nakanishi and coworkers reported the synthesis of Mo carbonitride (MoCN) nanomaterial [194]. The reaction of Na$_2$MoO$_4$ with diaminopyridine (DAP) in acidic condition gave DAP-bound Mo oxide, which was polymerized by NaHCO$_3$/NH$_4$H$_2$S$_2$O$_8$ as emitting CO$_2$ gas. The CO$_2$ emission step formed nano-sized (PDAP)-2H$^+$ /MoO$_2^{2-}$ (PDAP = poly-diaminopyridine) complex causing a high density of the catalytically active site. Finally, the polymer was pyrolyzed at 800 °C to become MoCN nanomaterial (Figure 4f). MoCN nanomaterial showed the HER activity above −0.05 V vs. RHE and reached 10 mA/cm$^2$ at −0.14 V vs. RHE in sulfuric acid (pH 1) solution. MoCN nanomaterial had electrocatalytic stability during 1000 CV scans between −0.35 and 0.2 V vs. RHE.

Yu and coworkers used hybrid phosphorous-doped nanoporous carbon (PC) and RGO to support MoO$_2$ [195]. MoO$_2$@PC-RGO had a carbon skeleton, which prevented aggregation of catalytically active MoO$_2$ nanoparticles. Additionally, the synergistic combination of PC and RGO assisted to enhance the catalytic activity.

![Figure 4](image-url)

**Figure 4.** (a) STM image of atomically re-dissolved MoS$_2$ particle on Au(111) [170]; (b) electron micrograph of MoS$_3$-CV film on ITO [172]; (c) CV scan dependency of the mass of MoS$_{2+x}$ film [174]; (d) TEM images (TEM, Ori) and EDS mapping of Mo carbonitride [194]; (e) synthetic process of Mo$_2$N/CeO$_2$@NF [196]; (f) polarization curves of Mo$_2$N/CeO$_2$@NF-0.05, 20 wt% Pt/C, CeO$_2$@NF and Mo$_2$N@NF [196]. Ref. [170] with permission from copyright 2007 American Association for the Advancement of Science, Ref. [172] with permission from the Royal Society of Chemistry, and Refs. [174,194,196] with permission from copyright American Chemical Society.

The use of adhesives for power-deposition on electrode generally lowers catalytic efficiency, so nickel foam (NF) has been used to prepare self-supported electrode. Huang and coworkers used NF to support Mo$_2$N/CeO$_2$ hetero-nanoparticles (Figure 4d) [196]. CeO$_2$ was coated on NF by hydrothermal method, and the CeO$_2$-fabricated NF was covered by Mo$_2$N with varying amounts of (NH$_4$)$_4$Mo$_7$O$_{24}$·4H$_2$O (0.02, 0.04, 0.05, 0.06 mmol) precursor by solvothermal method. Post-annealing at 500 °C for 5 h under NH$_3$ atmosphere afforded Mo$_2$N/CeO$_2$@NF. The synthetic condition using 0.05 mmol Mo source gave the best HER activity. Mo$_2$N/CeO$_2$@NF-0.05 sample showed smaller overpotential than commercial 20 wt% Pt/C. The high catalytic activity was probably because electronic interaction between Mo$_2$N and CeO$_2$ lowers the energy barrier for hydrogen intermediate formation (Figure 4e). The catalytic efficiencies of the above Mo-based HER electrocatalysts are compared in Table 3.
5. Heterogeneous Mo-Containing O₂-Evolution Electro catalysts

Water splitting is an ideal method for the conversion of electric and solar energy to the chemical bond energy of dihydrogen. However, oxidation of water to O₂, the counterpart reaction of H₂ evolution, is kinetically slow, which decreases the overall efficiency of the water-splitting reaction. Since oxygen evolution reaction (OER) is a multi-electron process demanding large overpotential, efficient electrocatalysts are highly desired. RuO₂ is a benchmark catalyst for the OER, but the high cost and easy decomposition to RuO₄ are drawbacks of using Ru. Research efforts have been made to develop Earth-abundant metal-based electrocatalysts with high-performance and durability, and, among those, Mo-containing electrocatalysts have shown promising OER activities.

MoS₂ edge site is also known to be active for the OER, and, thus, various synthetic methods were developed to enlarge the edge site area. Mohanty and coworkers investigated the OER activity of MoS₂ quantum dots [197]. The MoS₂ quantum dot compounds (MSQDs) of 2–5 nm size were synthesized without aggregation through single-step hydrothermal reaction using (NH₄)₂MoS₄ precursor (Figure 5a,b). Repeating linear sweep
Catalysts 2021, 11, 217

voltaammetry (LSV) scans up to 50 cycles increased the OER current density, because the electrochemically active surface area of MSQDs was enlarged with the potential scans.

Direct growing methods, useful to increase contact, conductivity, and electron transfer, are generally applied to prepare OER electrocatalysts. In 2016, Yan and Lu prepared a porous MoS$_2$ microsphere on nickel foam (NF) [198]. The MoS$_2$ on NF showed a higher catalytic rate (105 mV/dec Tafel slope) than commercial RuO$_2$ on NF (127 mV/dec) and 20% Pt/C (150 mV dec$^{-1}$). Cui and coworkers synthesized mesoporous MoO$_3$ nanosheets on NF [199]. The mesoporosity of MoO$_2$ enlarged the active surface area and slightly improved the catalytic activity than that of compact MoO$_2$.

Borde increases a reverse electron transfer to the metal site, which accordingly increases electron density on the catalytic site. Gupta and coworkers synthesized ternary Co-Mo-B hetero-metal nanocomposite, which gave enhanced OER activity [200]. Li and coworkers used a well-defined Cu nanowire to deposit Ni/Mo-alloy catalyst [201]. Alkaline anodization and subsequent cathodic reduction process modified the surface of Cu foam. A mixture of Ni(SO$_4$)$_2$ and Na$_2$MoO$_4$ were electrodeposited on the Cu nano-scaffold to obtain Ni-Mo/Cu nanowire. The Ni-Mo/Cu nanowire exhibited comparable OER activity with commercial Pt/C (RuO$_2$) on Cu foam.

Yang and coworkers examined the synergistic effect of trimetallic FeCoMo nanocomposite for the OER test [202]. Amorphous FeCoMo nanocomposite was synthesized as a rod-like shape by hydrolysis of a mixture of CoCl$_2$·6H$_2$O, FeCl$_3$·6H$_2$O and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, hexamethylene tetramine at 90 °C. The existence of high-valent Mo$^{6+}$ was characterized by Raman spectroscopy. In situ X-ray absorption near edge structure (XANES) showed that Mo$^{6+}$ tends to attract electrons from 3d transition metals, which possibly promoted the OER process.

Gao and coworkers prepared a bifunctional catalyst using MoS$_2$ HER catalyst and Ni$_3$S$_2$ OER catalyst (Figure 5c-e) [203]. MoS$_2$–Ni$_3$S$_2$ heteronanorods on NF afforded higher OER activity than Ni$_3$S$_2$/NF and MoS$_2$/NF.

The bimetallic system enables manipulation of electronic structure and gives abundant active sites, but a synthesis of pure phase is difficult. Lan and coworkers could make pure-phase bimetallic Co/Mo carbides using mesoporous carbon substrate (Figure 5f) [204]. Transition metal carbide also gave the high catalytic activity because of the good electrical conductivity, metallic property, and chemical stability.

Ni oxyhydroxide is an active site for OER, but the low stability decreases the catalytic efficiency. Shen and coworkers increased the stability by fabricating MoFe:Ni(OH)$_2$/NiOOH nanosheet and studied synergistic effect [205].

Ma and coworkers synthesized one-dimensional MoO$_2$-Co$_2$Mo$_3$O$_8$@C nanorods with the enlarged catalytic surface area [206]. The ZIF-67 MOF was attached to MoO$_2$ nanorods to form MoO$_3$@ZIF-67, and subsequent hydrothermal reaction at 700 °C gave MoO$_2$-Co$_2$Mo$_3$O$_8$@C nanorods (containing Co/Mo in 9.1/10.5% ratio). The organic ligand of ZIF-67 was carbonized into carbon, which served as a reductant to reduce excess MoO$_3$ to MoO$_2$. The MoO$_2$-Co$_2$Mo$_3$O$_8$@C nanorods showed similar activity as the benchmark RuO$_2$.

Yang and coworkers studied the OER activity of Ni$_2$Mo$_3$N hetero-metal nitride [207]. They reported that an amorphous surface oxygen-rich activation layer (SOAL) was generated on Ni$_2$Mo$_3$N nanoparticle surface by applying high oxidative potential in alkaline conditions. The computational study suggested that SOAL could increase the OER activity, because the conjugation of Ni-nitrides active sites and the secondary Mo-electron pump promoted the catalytic reaction.

Jiang and coworkers reported the synergistic effect of Co$_3$Mo alloy nanoparticles as attached to nanoporous Cu skeleton [208]. They synthesized Mo-doped Co$_3$O$_4$ nanoflakes on CuO/Cu skeleton by electro-oxidation (EO) at 1.57 V vs. RHE. The EO Co$_3$Mo/Cu showed lower OER onset overpotential than Ir/C supported by nanoporous Cu. Since Co$_3$Mo/Cu also acted as a highly active HER catalyst, they composed a water electrolysis set-up by Co$_3$Mo/Cu cathode and EO Co$_3$Mo/Cu anode. The Co$_3$Mo/Cu-based electrolyzer showed overall water splitting delivering a current density of 100 mA/cm$^2$ at 1.62 V vs. RHE. The
water-splitting system acted more efficiently than Pt/C/Cu-Ir/C/Cu set-up (Figure 5g,h). The catalytic efficiency parameters of the Mo-based OER electrocatalysts are compared in Table 4.

![Image](https://via.placeholder.com/150)

**Figure 5.** (a,b) HRTEM images of MSQCs [197]; (c) EDS and elemental mapping of MoS$_2$-Ni$_3$S$_2$ heteronanorods [203]; (d) polarization curves and (e) Tafel slopes of NF, Ni$_3$S$_2$/NF, MoS$_2$-Ni$_3$S$_2$ HNRs/NF, and Pt/C on NF and MoS$_2$/NF [203]; (f) overpotentials of IrO$_2$ and Co/Mo carbides (Co$_6$Mo$_6$C$_2$/NCRGO with different Co/Mo ratios 1:1, 2:1, 3:1) at 10 mA/cm$^2$ [204]; (g) polarization curves of EO Co$_3$Mo/Cu, EO Co/Cu, EO Cu, and Ir/C/Cu (Inset: SEM image of EO Co$_3$Mo/Cu) [208]; and (h) polarization curves for electrocatalytic water splitting of nanoporous Co$_3$Mo/Cu and EO Co$_3$Mo/Cu electrodes, nanoporous NiFe/Cu and EO NiFe/Cu electrodes and Pt/C/Cu and Ir/C/Cu. Inset: Comparison of current density at 1.65 V [208]. Reproduced from Refs. [197,203,204] with permission from copyright American Chemical Society and Ref. [208] with permission from copyright 2020 Springer Nature.

| Catalyst                          | Current Density (mA/cm$^2$) | Overpotential (mV) | Tafel Slope (mV/dec) | Ref.     |
|-----------------------------------|-----------------------------|--------------------|----------------------|----------|
| MoS$_2$ on NF                     | 20                          | 310 mV             | 105                  | [198]    |
| Mesoporous MoO$_2$ nanosheets on NF| 10                          | 260 mV             | 54                   | [199]    |
| Co-Mo-B                           | 10                          | 320 mV             | 56                   | [200]    |
| Ni-Mo/Cu nanowire                 | 20                          | 280 mV             | 66                   | [201]    |
| FeCoMo nanocomposite              | 10                          | 277 mV             | 27.74                | [202]    |
| MoS$_2$-Ni$_3$S$_2$ heteronanorods| 10                          | 249 mV             | 57                   | [203]    |
| bimetallic Co/Mo carbides         | 10                          | 260 mV             | 50                   | [204]    |
| MoFe:Ni(OH)$_2$/NiOOH nanosheet   | 100                         | 280 mV             | 47                   | [205]    |
| MSQDs-AC                          | 10                          | 370 mV             | 39                   | [197]    |
| MoO$_2$-Co$_2$Mo$_3$O$_6$@C nanorods| 10                          | 320 mV             | 88                   | [206]    |
| Ni$_2$Mo$_3$N hetero-metal nitride| 10                          | 270 mV             | 59                   | [207]    |
| EO Co$_3$Mo alloy nanoparticles   | 164                         | 350 mV             | 82                   | [208]    |

### 6. Conclusions

This review summarizes Mo-containing metalloenzymes and their model complexes, homogeneous and heterogeneous catalysts under categories of reactivities with CO$_2$, N$_2$, H$_2$, and O$_2$. Compared to the Mo enzymes, catalytic activities of synthetic systems remain at a low-efficiency level. Thus, continuous research efforts in synthetic and theoretical perspectives are requested to achieve high-performing catalysts. The revealed Mo-enzyme
structures enabled synthetic research on the enzyme reactivities, and concomitant theoretical studies gave an in-depth understanding of the enzyme mechanism. However, previously proposed mechanisms need further supports by synthetic experiments, and spectroscopic research on living cells still has limitations; thus, more active modeling studies are required.

Along with the modeling studies, new catalysts by ligand design should be developed to find an optimal condition to prepare active Mo ion. Ligand design for a low-valent Mo ion to function under lower gas pressure is pursued. Examples of homogeneous catalysts using high-valent Mo ions are relatively rare. Mimicking the enzyme active site partially or conceptually could provide synthetic ideas to develop both low- and high-valent Mo-based catalysts. In addition, catalytic stability of the Mo complex is a prerequisite for commercialization. Utilization of hetero-metallic surface is a method of preventing deactivation of catalytic sites as well as providing synergistic effects. Another method would be to use polymer or organic scaffold for regulating access of reagents into a catalytic site, which is similar to the enzymatic strategy to protect the active site by surrounding it with polypeptide chains.

Funding: This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2020R1C1C1007106) and GIST Research Institute (GRI) grant funded by the GIST in 2020.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. van der Ham, C.J.M.; Koper, M.T.M.; Hetterscheid, D.G.H. Challenges in reduction of dinitrogen by proton and electron transfer. Chem. Soc. Rev. 2014, 43, 5183–5191. [CrossRef] [PubMed]
2. John, J.; Lee, D.-K.; Sim, U. Photocatalytic and electrocatalytic approaches towards atmospheric nitrogen reduction to ammonia under ambient conditions. Nano Converg. 2019, 6, 15. [CrossRef]
3. He, M.; Sun, Y.; Han, B. Green Carbon Science: Scientific Basis for Integrating Carbon Resource Processing, Utilization, and Recycling. Angew. Chem. Int. Ed. 2013, 52, 9620–9633. [CrossRef]
4. Zou, X.; Zhang, Y. Noble metal-free hydrogen evolution catalysts for water splitting. Chem. Soc. Rev. 2015, 44, 5148–5180. [CrossRef] [PubMed]
5. Walter, M.G.; Warren, E.L.; McKone, J.R.; Boettcher, S.W.; Mi, Q.; Santori, E.A.; Lewis, N.S. Solar Water Splitting Cells. Chem. Rev. 2010. [CrossRef] [PubMed]
6. Rosca, V.; Duca, M.; de Groot, M.T.; Koper, M.T.M. Nitrogen Cycle Electrocatalysis. Chem. Rev. 2009, 109, 2209–2244. [CrossRef] [PubMed]
7. Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S.Z. Design of electrocatalysts for oxygen- and hydrogen-involving energy conversion reactions. Chem. Soc. Rev. 2015, 44, 2060–2086. [CrossRef]
8. Janani, G.; Choi, H.; Surendran, S.; Sim, U. Recent advances in rational design of efficient electrocatalyst for full water splitting across all pH conditions. MRS Bull. 2020, 45, 539–547. [CrossRef]
9. Andreini, C.; Bertini, I.; Cavallaro, G.; Holliday, G.L.; Thornton, J.M. Metal ions in biological catalysis: From enzyme databases to general principles. J. Biol. Inorg. Chem. 2008, 13, 1205–1218. [CrossRef]
10. Bullock, R.M.; Chen, J.G.; Gagliardi, L.; Chirik, P.J.; Farha, O.K.; Hendon, C.H.; Jones, C.W.; Keith, J.A.; Klosin, J.; Minteer, S.D.; et al. Using nature’s blueprint to expand catalysis with Earth-abundant metals. Science 2020, 369. [CrossRef]
11. Eckenhoff, W.T.; Brennessel, W.W.; Eisenberg, R. Light-Driven Hydrogen Production from Aqueous Protons using Molybdenum Catalysts. Inorg. Chem. 2014, 53, 9860–9869. [CrossRef]
12. Dos Santos, P.C.; Dean, D.R.; Hu, Y.; Ribbe, M.W. Formation and Insertion of the Nitrogenase Iron–Molybdenum Cofactor. Chem. Rev. 2004, 104, 1159–1174. [CrossRef]
13. Dobnik, H. Structural aspects of mononuclear Mo/W-enzymes. Coord. Chem. Rev. 2011, 255, 1104–1116. [CrossRef]
14. Cordas, C.M.; Moura, J.J.G. Molybdenum and tungsten enzymes redox properties—A brief overview. Coord. Chem. Rev. 2019, 394, 53–64. [CrossRef]
15. Lin, Y.-W. Rational Design of Artificial Metallocproteins and Metalloenzymes with Metal Clusters. Molecules 2019, 24, 2743. [CrossRef] [PubMed]
16. Zhou, J.; Hu, L.; Zhao, P.; Lee, Y.S.; Wong, K.-Y. Recent Advances in Electrocatalytic Hydrogen Evolution Using Nanoparticles. Chem. Rev. 2020. [CrossRef] [PubMed]
17. Yang, L.; Liu, P.; Li, J.; Xiang, B. Two-Dimensional Material Molybdenum Disulfides as Electrocatalysts for Hydrogen Evolution. Catalysts 2017, 7, 285. [CrossRef]
18. Zhang, S.; Fan, Q.; Xia, R.; Meyer, T.J. CO₂ Reduction: From Homogeneous to Heterogeneous Electrocatalysis. Acc. Chem. Res. 2020, 53, 255–264. [CrossRef]
19. Axley, M.J.; Grahame, D.A. Kinetics for formate dehydrogenase of Escherichia coli formate-hydrogenlyase. J. Biol. Chem. 1991, 266, 13731–13736. [CrossRef]
20. Appel, A.M.; Bercaw, J.E.; Bocarsly, A.B.; Dobbeck, H.; DuBois, D.L.; Dupuis, M.; Ferry, J.G.; Fujita, E.; Hille, R.; Kenis, P.J.A.; et al. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO₂ Fixation. Chem. Rev. 2013, 113, 6621–6658. [CrossRef]
21. Hille, R.; Hall, J.; Basu, P. The Mononuclear Molybdenum Enzymes. Chem. Rev. 2014, 114, 3963–4038. [CrossRef]
22. Hartmann, T.; Leimbähler, S. The oxygen-tolerant and NAD⁺-dependent formate dehydrogenase from Rhodobacter capsulatus is able to catalyze the reduction of CO₂ to formate. FEBS J. 2013, 280, 6083–6096. [CrossRef]
23. Maia, L.B.; Fonseca, L.; Moura, I.; Moura, J.J.G. Reduction of Carbon Dioxide by a Molybdenum-Containing Formate Dehydrogenase: A Kinetic and Mechanistic Study. J. Am. Chem. Soc. 2016, 138, 8834–8846. [CrossRef] [PubMed]
24. Boyington, J.C.; Gladyshev, V.N.; Khangulov, S.V.; Stadtman, T.C.; Sun, P.D. Crystal structure of formate dehydrogenase H: Catalysis involving Mo, molybdopterin, selenocysteine, and an Fe₄S₄ cluster. Science 1997, 275, 1305–1308. [CrossRef] [PubMed]
25. Raaijmakers, H.C.A.; Romao, M.J. Formate-reduced E-coli formate dehydrogenase H: The reinterpretation of the crystal structure suggests a new reaction mechanism. J. Biol. Inorg. Chem. 2006, 11, 849–854. [CrossRef]
26. Mota, C.S.; Rivas, M.G.; Brondino, C.D.; Moura, I.; Moura, J.J.G.; Gonzalez, P.J.; Cerqueira, N.M.F.S.A. The mechanism of formate oxidation by metal-dependent formate dehydrogenase. J. Biol. Inorg. Chem. 2011, 16, 1255–1268. [CrossRef]
27. Cerqueira, N.M.F.S.A.; Fernandes, P.A.; Gonzalez, P.J.; Moura, J.J.G.; Ramos, M.J. The Sulfur Shift: An Activation Mechanism for Periplasmic Nitrate Reductase and Formate Dehydrogenase. Inorg. Chem. 2013, 52, 10766–10772. [CrossRef] [PubMed]
28. Schrapers, P.; Hartmann, T.; Kosiţzki, R.; Dau, H.; Reschke, S.; Schulzke, C.; Leimbähler, S.; Haumann, M. Sulphido and Cysteine Ligation Changes at the Molybdenum Cofactor during Substrate Conversion by Formate Dehydrogenase (FDH) from Rhodobacter capsulatus. Inorg. Chem. 2015, 54, 3260–3271. [CrossRef]
29. Duffus, B.R.; Schrapers, P.; Schuth, N.; Mebs, S.; Dau, H.; Leimbähler, S.; Haumann, M. Anion Binding and Oxidative Modification at the Molybdenum Cofactor of Formate Dehydrogenase from Rhodobacter capsulatus Studied by X-ray Absorption Spectroscopy. Inorg. Chem. 2020, 59, 214–225. [CrossRef]
30. Hille, R.; Dingwall, S.; Wilcoxen, J. The aerobic CO dehydrogenase from Oligotropha carboxidovorans. J. Biol. Inorg. Chem. 2015, 20, 243–251. [CrossRef]
31. Dobbeck, H.; Gremer, L.; Kiefer, R.; Huber, R.; Meyer, O. Catalysis at a dinuclear [CuSMo(=O)OH] cluster in a CO oxidation by metal-dependent formate dehydrogenase. J. Biol. Inorg. Chem. 2011, 16, 1255–1268. [CrossRef]
32. Cerqueira, N.M.F.S.A.; Fernandes, P.A.; Gonzalez, P.J.; Moura, J.J.G.; Ramos, M.J. The Sulfur Shift: An Activation Mechanism for Periplasmic Nitrate Reductase and Formate Dehydrogenase. Inorg. Chem. 2013, 52, 10766–10772. [CrossRef] [PubMed]
33. Fogeron, T.; Porcher, J.-P.; Gomez-Mingot, M.; Chamoreau, L.-M.; Mellot-Draznieks, C.; Li, Y.; Fontecave, M. A Bioinspired Nickel(bis-dithiolene) Complex as a Homogeneous Catalyst for Carbon Dioxide Electroreduction. ACS Catal. 2018, 8, 2030–2038. [CrossRef]
34. Foger, T.; Todorova, T.K.; Porcher, J.-P.; Gomez-Mingot, M.; Chamoreau, L.-M.; Mellot-Draznieks, C.; Li, Y.; Fontecave, M. A Bioinspired Nickel(bis-dithiolene) Complex as a Homogeneous Catalyst for Carbon Dioxide Electroreduction. Angew. Chem. Int. Ed. 2018, 57, 17033–17037. [CrossRef] [PubMed]
35. Mouchfiq, A.; Todorova, T.K.; Dey, S.; Fontecave, M.; Mougel, V. A bioinspired molybdenum–copper molecular catalyst for CO₂ electroreduction. Chem. Sci. 2020, 11, 5503–5510. [CrossRef] [PubMed]
36. Chisholm, M.H.; Cotton, F.A.; Extine, M.W.; Reichert, W.W. The molybdenum-molybdenum triple bond Insertion reactions of hexakis(alkoxy)dimolybdenum compounds with carbon dioxide and single-crystal x-ray structural characterization of bis(tert-butylcarboxyco)tetrais(tert-butoxy)dimolybdenum. J. Am. Chem. Soc. 1978, 100, 1727–1734. [CrossRef]
Catalysts 2021, 11, 217

80. Bassegoda, A.; Madden, C.; Wakerley, D.W.; Reisner, E.; Hirst, J. Reversible Interconversion of CO$_2$ and CO into methanol: Visible-light induced photocatalytic reduction of carbon dioxide into methanol. *Carbon* 2015, *94*, 91–100. [CrossRef]

81. Yuan, M.; Sahin, S.; Cai, R.; Abdellaoui, S.; Hickey, D.P.; Minteer, S.D.; Milton, R.D. Creating a Low-Potential Redox Polymer for Electrocatalysis. *J. Phys. Chem. A* 2019, *94*, 4500–4507. [CrossRef]

82. Ferguson, S.J. Nitrogen cycle enzymology. *Curr. Opin. Chem. Biol.* 1998, *2*, 182–193. [CrossRef]

83. Raymond, J.; Siefert, J.L.; Staples, C.R.; Blankenship, R.E. The Natural History of Nitrogen Fixation. *Environmental Science & Technology* 2012, *46*, 2983–3012. [CrossRef]

84. Raymond, J.; Siefert, J.L.; Staples, C.R.; Blankenship, R.E. The Natural History of Nitrogen Fixation. *Environmental Science & Technology* 2012, *46*, 2983–3012. [CrossRef]

85. Raymond, J.; Siefert, J.L.; Staples, C.R.; Blankenship, R.E. The Natural History of Nitrogen Fixation. *Environmental Science & Technology* 2012, *46*, 2983–3012. [CrossRef]

86. Xu, J.; Li, X.; Liu, W.; Sun, Y.; Ju, Z.; Yao, T.; Wang, C.; Ju, H.; Zhu, J.; Wei, S.; et al. Carbon Dioxide Electroreduction into Syngas Boosted by a Partially Delocalized Charge in Molybdenum Sulfide Selenide Alloy Monolayers. *Angew. Chem. Int. Ed.* 2017, *56*, 9121–9125. [CrossRef] [PubMed]

87. Wiig, J.A.; Hu, Y.; Lee, C.C.; Ribbe, M.W. Radical SAM-Dependent Carbon Insertion into the Nitrogenase M-Cluster. *Science* 2012, *337*, 337–340. [CrossRef] [PubMed]

88. Garagounis, I.; Kyriakou, V.; Skodra, A.; Vasileiou, E.; Stoukides, M. Electrochemical Synthesis of Ammonia in Solid Electrolyte Membranes. *Angew. Chem. Int. Ed.* 2012, *51*, 2387–2402. [CrossRef] [PubMed]

89. Jia, H.-P.; Quadrelli, E.A. Mechanistic aspects of dinitrogen cleavage and hydrogenation to produce ammonia in catalysis and photosynthesis systems. *Chem. Rev.* 2014, *114*, 4041–4062. [CrossRef]

90. MacKay, B.A.; Fryzuk, M.D. Nitrogen Coordination Chemistry: On the Biomimetic Borderlands. *Chem. Rev.* 2004, *104*, 385–402. [CrossRef]

91. Deng, H.; Hoffmann, R. How N2 Might Be Activated by the FeMo-Cofactor in Nitrogenase. *Angew. Chem. Int. Ed.* 1993, *32*, 1062–1065. [CrossRef]

92. Burgess, B.K.; Lowe, D.J. Mechanism of Molybdenum Nitrogenase. *Chem. Rev.* 1996, *96*, 2983–3012. [CrossRef]

93. Howard, J.B.; Rees, D.C. Structural Basis of Biological Nitrogen Fixation. *Chem. Rev.* 1996, *96*, 2965–2982. [CrossRef]

94. Hoffman, B.M.; Lukoyanov, D.; Yang, Z.-Y.; Dean, D.R.; Seefeldt, L.C. Mechanism of Nitrogen Fixation by Nitrogenase: The Next Stage. *Chem. Rev.* 2011, *114*, 4041–4062. [CrossRef]

95. Spatzal, T.; Aksoyoglu, M.; Zhang, L.; Andrade, S.L.A.; Schleicher, E.; Weber, S.; Rees, D.C.; Einsle, O. Evidence for Intersitial Carbon in Nitrogenase FeMo Cofactor. *Science* 2011, *334*, 940. [CrossRef]

96. Lancaster, K.M.; Roemelt, M.; Ettenhuber, P.; Hu, Y.; Ribbe, M.W.; Neese, F.; Bergmann, U.; DeBeer, S. X-ray Emission Spectroscopy Evidences a Central Carbon in the Iron-Molybdenum Cofactor. *Science* 2011, *334*, 974. [CrossRef] [PubMed]

97. Wiig, J.A.; Hu, Y.; Lee, C.C.; Ribbe, M.W. Radical SAM-Dependent Carbon Insertion into the Nitrogenase M-Cluster. *Science* 2012, *337*, 1672. [CrossRef]

98. Wolff, T.E.; Berg, J.M.; Warrick, C.; Hodgson, K.O.; Holm, R.H.; Frankel, R.B. The molybdenum-iron-sulfur cluster complex [Mo$_2$Fe$_3$(SC$_2$H$_5$)$_6$]$^{1-}$. A synthetic approach to the molybdenum site in nitrogenase. *J. Am. Chem. Soc.* 1978, *100*, 4630–4632. [CrossRef]
Catalysts 2021, 11, 217

99. Wolff, T.E.; Berg, J.M.; Hodgson, K.O.; Frankel, R.B.; Holm, R.H. Synthetic approaches to the molybdenum site in nitrogenase. Preparation and structure of the molybdenum-iron-sulfur "double-cubane" cluster complexes \([\text{Mo}_2\text{Fe}_4\text{S}_8(\text{SC}_2\text{H}_4\text{S})_4]^{3-}\) and \([\text{Mo}_2\text{Fe}_4\text{S}_8(\text{SC}_2\text{H}_4\text{S})_2]^{3-}\). J. Am. Chem. Soc. 1979, 101, 4140–4150. [CrossRef]

100. Armstrong, W.H.; Holm, R.H. Synthesis and structure of a new type of molybdenum-iron-sulfur double-cubane cluster and evidence for formation of magnetically uncoupled \(S = 3/2\) MoFe\(_2\)S\(_4\) subclusters. J. Am. Chem. Soc. 1981, 103, 6246–6248. [CrossRef]

101. Armstrong, W.H.; Mascharak, P.K.; Holm, R.H. Doubly bridged double cubanes containing MFe\(_2\)S\(_4\) clusters \((M = \text{Mo, W})\). Synthesis, structure, and conversion to spin-quartet single clusters in solution. J. Am. Chem. Soc. 1982, 104, 4373–4383. [CrossRef]

102. Cramer, S.P.; Gillum, W.O.; Hodgson, K.O.; Mortenson, L.E.; Stiefel, E.I.; Chisnell, J.R.; Brill, W.J.; Shah, V.K. The molybdenum site in nitrogenase. Acc. Chem. Res. 2001, 34, 955–962. [CrossRef]

103. Coucouvanis, D.; Demadis, K.D.; Kim, C.G.; Dunham, R.W.; Kampf, J.W. Single and double MoFe\(_2\)S\(_4\) clusters. J. Am. Chem. Soc. 2011, 133, 3814–3819. [CrossRef] [PubMed]

104. Fomitchev, D.V.; McLauchlan, C.C.; Holm, R.H. Heterometal Cubane-Type MFe\(_2\)S\(_4\) Clusters \((M = \text{Mo, W})\) Trigonal Symmetrized with Hydrotris(pyrazolyl)borate(1−) Capping Ligands. Inorg. Chem. 2002, 41, 958–966. [CrossRef]

105. Bjørnsson, R.; Neese, F.; Schrock, R.R.; Einsle, O.; DeBeer, S. The discovery of Mo(III) in FeMoco: Reuniting enzyme and model chemistry. J. Biol. Inorg. Chem. 2004, 9, 939. [CrossRef]

106. Yang, J. Progress in Synthesizing Analogues of Nitrogenase Metalloclusters for Catalytic Reduction of Nitrogen to Ammonia. Catalysts 2019, 9, 939. [CrossRef]

107. Tanifuji, K.; Ohki, Y. Metal–Sulfur Compounds in N\(_2\) Reduction and Nitrogenase-Related Chemistry. Chem. Rev. 2020, 120, 5194–5251. [CrossRef]

108. Komori, K.; Oshita, H.; Mizobe, Y.; Hidai, M. Preparation and properties of molybdenum and tungsten dinitrogen complexes. J. Am. Chem. Soc. 1993, 115, 3344–3345. [CrossRef]

109. Yandulov, D.V.; Schrock, R.R. Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center. Science 2003, 301, 76. [CrossRef]

110. Yandulov, D.V.; Schrock, R.R. Reduction of Dinitrogen to Ammonia at a Well-Protected Reaction Site in a Molybdenum Triamidoamine Complex. J. Am. Chem. Soc. 2002, 124, 6252–6253. [CrossRef]

111. Foster, S.L.; Bakovic, S.I.P.; Duda, R.D.; Maheshwari, S.; Milton, R.D.; Minteer, S.D.; Janik, M.J.; Renner, J.N.; Greenlee, L.F. Catalysts for nitrogen reduction to ammonia. Nat. Catal. 2018, 1, 490–500. [CrossRef]

112. Schrock, R.R. Catalytic reduction of dinitrogen under mild conditions. Chem. Commun. 2003, 19, 2389–2391. [CrossRef]

113. Yandulov, D.V.; Schrock, R.R.; Rheingold, A.L.; Ceccarelli, C.; Davis, W.M. Synthesis and Reactions of Molybdenum Triamidoamine Complexes Containing Hexaisopropylterphenyl Substituents. Inorg. Chem. 2003, 42, 796–813. [CrossRef] [PubMed]

114. Rittleng, V.; Yandulov, D.V.; Weare, W.W.; Schrock, R.R.; Hock, A.S.; Davis, W.M. Molybdenum Triamidoamine Complexes that Contain Hexa-tert-butylterphenyl, Hexamethylterphenyl, or p-Bromohexaisopropylterphenyl Substituents. An Examination of Some Catalyst Variations for the Catalytic Reduction of Dinitrogen. J. Am. Chem. Soc. 2004, 126, 6150–6163. [CrossRef]

115. Schrock, R.R. Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center. Acc. Chem. Res. 2005, 38, 955–962. [CrossRef] [PubMed]

116. Yandulov, D.V.; Schrock, R.R. Studies Relevant to Catalytic Reduction of Dinitrogen to Ammonia by Molybdenum Triamidoamine Complexes. Inorg. Chem. 2005, 44, 1103–1117. [CrossRef]

117. Schrock, R.R. Reduction of dinitrogen. Proc. Natl. Acad. Sci. USA 2006, 103, 17087. [CrossRef]

118. Schrock, R.R. Catalytic Reduction of Dinitrogen to Ammonia by Molybdenum: Theory versus Experiment. Angew. Chem. Int. Ed. 2008, 47, 5512–5522. [CrossRef]

119. Tanaka, H.; Sasada, A.; Kouno, T.; Yuki, M.; Miyake, Y.; Nakashima, H.; Nishibayashi, Y.; Yoshizawa, K. Molybdenum-Catalyzed Transformation of Molecular Dinitrogen into Silylamine: Experimental and DFT Study on the Remarkable Role of Ferrocenylidiphosphine Ligands. J. Am. Chem. Soc. 2011, 133, 3498–3506. [CrossRef]

120. Arashiba, K.; Miyake, Y.; Nishibayashi, Y. A molybdenum complex bearing PNP-type pincer ligands leads to the catalytic reduction of dinitrogen into ammonia. Nat. Chem. 2011, 3, 120–125. [CrossRef]

121. Nishibayashi, Y. Molybdenum-catalyzed reduction of molecular dinitrogen under mild reaction conditions. Dalton Trans. 2012, 41, 7447–7453. [CrossRef]

122. Kuriyama, S.; Arashiba, K.; Nakajima, K.; Tanaka, H.; Kamaru, N.; Yoshizawa, K.; Nishibayashi, Y. Catalytic Formation of Ammonia from Molecular Dinitrogen by Use of Dinitrogen-Bridged Dimolybdenum–Dinitrogen Complexes Bearing PNP-Pincer Ligands: Remarkable Effect of Substituent at PNP-Pincer Ligand. J. Am. Chem. Soc. 2014, 136, 9719–9731. [CrossRef]

123. Kuriyama, S.; Arashiba, K.; Nakajima, K.; Tanaka, H.; Yoshizawa, K.; Nishibayashi, Y. Nitrogen fixation catalyzed by ferrocene-substituted dinitrogen-bridged dimolybdenum–dinitrogen complexes: Unique behavior of ferrocene moiety as redox active site. Chem. Sci. 2015, 6, 3940–3951. [CrossRef]
124. Itabashi, T.; Mori, I.; Arashiba, K.; Eizawa, A.; Nakajima, K.; Nishibayashi, Y. Effect of substituents on molybdenum triiodide complexes bearing PNP-type pincer ligands toward catalytic nitrogen fixation. *Dalton Trans.* 2019, 48, 3182–3186. [CrossRef] [PubMed]

125. Arashiba, K.; Eizawa, A.; Tanaka, H.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Catalytic Nitrogen Fixation via Direct Cleavage of Nitrogen–Nitrogen Triple Bond of Molecular Dinitrogen under Ambient Reaction Conditions. *Bull. Chem. Soc. Jpn.* 2017, 90, 1111–1118. [CrossRef]

126. Eizawa, A.; Arashiba, K.; Egi, A.; Tanaka, H.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Catalytic Reactivity of Molybdenum–Trihalide Complexes Bearing PNP-Type Pincer Ligands. *Chem. Asian J.* 2019, 14, 2091–2096. [CrossRef] [PubMed]

127. Ashida, Y.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. Molybdenum-catalysed ammonia production with samarium diiodide and alcohols or water. *Nature 2019*, 568, 536–540. [CrossRef]

128. Brown, K.A.; Harris, D.F.; Wilker, M.B.; Rasmussen, A.; Khadka, N.; Hambly, H.; Keable, S.; Dukovic, G.; Peters, J.W.; Seefeldt, L.C.J.S. Light-driven dinitrogen reduction catalyzed by a CdS: Nitrogenase MoFe protein biohybrid. *Science 2016*, 352, 448–450. [CrossRef]

129. Nazemi, M.; Panikkannavalappil, S.R.; El-Sayed, M.A. Enhancing the rate of electrochemical nitrogen reduction reaction for ammonia synthesis under ambient conditions using hollow gold nanocages. *Nano Energy 2018*, 49, 316–323. [CrossRef]

130. Manjunatha, R.; Schechter, A. Electrochemical synthesis of ammonia using ruthenium–platinum alloy at ambient pressure and low temperature. *Electrochem. Commun. 2018*, 90, 96–100. [CrossRef]

131. Tao, H.; Choi, C.; Ding, L.-X.; Jiang, Z.; Han, Z.; Jia, M.; Fan, Q.; Gao, Y.; Wang, H.; Robertson, A.W.; et al. Nitrogen Fixation by Ru Single-Atom Electrocatalytic Reduction. *Chem 2019*, 5, 204–214. [CrossRef]

132. Liu, H.-M.; Han, S.-H.; Zhao, Y.; Zhu, Y.-Y.; Tian, X.-L.; Zeng, J.-H.; Jiang, J.-X.; Xia, B.Y.; Chen, Y. Surfactant-free atomically ultrathin rhodium nanosheet nanoassemblies for efficient nitrogen electroreduction. *J. Mater. Chem. A 2018*, 6, 3211–3217. [CrossRef]

133. Huang, H.; Xia, L.; Shi, X.; Asiri, A.M.; Sun, X. Ag nanosheets for efficient electrocatalytic N₂ fixation to NH₃ under ambient conditions. *Chem. Commun. 2018*, 54, 11430–11433. [CrossRef]

134. Oshikiri, T.; Ueno, K.; Misawa, H. Selective Dinitrogen Conversion to Ammonia Using Water and Visible Light through Plasmon-induced Charge Separation. *Angew. Chem. Int. Ed. 2016*, 55, 3942–3946. [CrossRef]

135. Wang, H.; Li, Y.; Li, C.; Deng, K.; Wang, Z.; Xu, Y.; Li, X.; Xue, H.; Wang, L. One-pot synthesis of bi-metallic PdRu tripods as an efficient catalyst for electrocatalytic nitrogen reduction to ammonia. *J. Mater. Chem. A 2019*, 7, 801–805. [CrossRef]

136. Montoya, J.H.; Tsai, C.; Vojvodic, A.; Nørskov, J.K. The Challenge of Electrochemical Ammonia Synthesis: A New Perspective on Nitrogenase Bioelectrocatalysis: ATP-Independent Ammonia Production Using a Redox Polymer/MoFe Protein System. *ACS Catal. 2020*, 10, 6854–6861. [CrossRef]
Catalysts 2021, 11, 217

149. Badalyan, A.; Yang, Z.-Y.; Seefeldt, L.C. A Voltammetric Study of Nitrogenase Catalysis Using Electron Transfer Mediators. ACS Catal. 2019, 9, 1366–1372. [CrossRef]

150. Jensen, B.B.; Burris, R.H. Nitrous oxide as a substrate and as a competitive inhibitor of nitrogenase. Biochemistry 1986, 25, 1083–1088. [CrossRef]

151. Davis, L.C. Hydrazine as a substrate and inhibitor of Azotobacter vinelandii nitrogenase. Arch. Biochem. Biophys. 1980, 204, 270–276. [CrossRef]

152. Vaughn, S.A.; Burgess, B.K. Nitrite, a new substrate for nitrogenase. Biochemistry 1989, 28, 419–424. [CrossRef] [PubMed]

153. Hosseini, S.E.; Wahid, M.A. Hydrogen production from renewable and sustainable energy resources: Promising green energy carrier for clean development. Renew. Sustain. Energy Rev. 2016, 57, 850–866. [CrossRef]

154. Vrubel, H.; Hu, X. Growth and Activation of an Amorphous Molybdenum Sulfide Hydrogen Evolving Catalyst. J. Phys. Chem. Lett. 2015, 6, 951–957. [CrossRef]

155. Shi, Y.; Zhang, B. Recent advances in transition metal phosphide nanomaterials: Synthesis and applications in hydrogen evolution reaction. Chem. Soc. Rev. 2016, 45, 1529–1541. [CrossRef]

156. Kong, D.; Cha, J.J.; Wang, H.; Lee, H.R.; Cui, Y. First-row transition metal dichalcogenide catalysts for hydrogen evolution reaction. Energy Environ. Sci. 2013, 6, 3553–3558. [CrossRef]

157. Darenbourg, D.J.; Reibenspies, J.H.; Lai, C.-H.; Lee, W.-Z.; Darenbourg, M.Y. Analysis of an Organometallic Iron Site Model for the Heterodimetallic Unit of [NiFe]Hydrogenase. J. Am. Chem. Soc. 1997, 119, 7903–7904. [CrossRef]

158. Donovan, E.S.; Felton, G.A.N. Electrochemical analysis of cyclopentadienylmetal carbonyl dimer complexes: Insight into the design of hydrogen-producing electrocatalysts. J. Organomet. Chem. 2012, 711, 25–34. [CrossRef]

159. Karunadasa, H.I.; Chang, C.J.; Long, J.R. A molecular molybdenum-oxo catalyst for generating hydrogen from water. J. Am. Chem. Soc. 1980, 102, 7456–7461. [CrossRef]

160. DuBois, M.R.; VanDerveer, M.C.; DuBois, D.L.; Haltiwanger, R.C.; Miller, W.K. Characterization of reactions of hydrogen with coordinated sulfido ligands. J. Am. Chem. Soc. 2010, 132, 464–470. [CrossRef]

161. Appel, A.M.; DuBois, D.L.; Rakowski DuBois, M. Molybdenum–Sulfur Dimers as Electrocatalysts for the Production of Hydrogen at Low Overpotentials. J. Am. Chem. Soc. 2005, 127, 12717–12726. [CrossRef]

162. Jaramillo, T.F.; Bonde, J.; Nielsen, J.H.; Horch, S.; Chorkendorff, I.; Nørskov, J.K. Biomimetic Edge Site Mimic for Catalytic Hydrogen Generation. Science 2012, 335, 698. [CrossRef] [PubMed]

163. Vrubel, H.; Merki, D.; Hu, X. Hydrogen evolution catalyzed by MoS2 Nanoparticles as Catalyst for Hydrogen Evolution. J. Am. Chem. Soc. 2005, 127, 5308–5309. [CrossRef]

164. Jaramillo, T.F.; Jørgensen, K.P.; Bonde, J.; Nielsen, J.H.; Horch, S.; Chorkendorff, I. Identification of Active Edge Sites for Electrochemical H2 Evolution from MoS2 Nanocatalysts. Science 2007, 317, 100. [CrossRef]

165. Hinnemann, B.; Moses, P.G.; Bonde, J.; Jørgensen, K.P.; Nielsen, J.H.; Horch, S.; Chorkendorff, I. Biomimetic Hydrogen Evolution: MoS2 Nanoparticles as Catalyst for Hydrogen Evolution. J. Am. Chem. Soc. 2005, 127, 5308–5309. [CrossRef]

166. Merki, D.; Fierro, S.; Vrubel, H.; Hu, X. Amorphous molybdenum sulfide films as catalysts for electrochemical hydrogen production in water. Chem. Sci. 2011, 2, 1262–1267. [CrossRef]

167. Merki, D.; Fierro, S.; Vrubel, H.; Hu, X. Growth and Activation of an Amorphous Molybdenum Sulfide Hydrogen Evolving Catalyst. ACS Catal. 2013, 3, 2002–2011. [CrossRef]

168. Vrubel, H.; Hu, X. Hydrogen evolution catalyzed by MoS2 and MoS2 particles. Energy Environ. Sci. 2012, 5, 6136–6144. [CrossRef]

169. Vrubel, H.; Hu, X. Growth and Activation of an Amorphous Molybdenum Sulfide Hydrogen Evolving Catalyst. ACS Catal. 2013, 3, 2002–2011. [CrossRef]

170. Jaramillo, T.F.; Bonde, J.; Zhang, J.; Ooi, B.-L.; Andersson, K.; Ulstrup, J.; Chorkendorff, I. Hydrogen Evolution on Supported Incomplete Cubane-type [Mo5S13]4+ Electrocatalysts. J. Phys. Chem. C 2008, 112, 17492–17498. [CrossRef]

171. Kibsgaard, J.; Jaramillo, T.F.; Besenbacher, F. Building an appropriate active-site motif into a hydrogen-evolution catalyst with thiomolybdate [Mo3S13]2− clusters. Nat. Chem. 2014, 6, 248–253. [CrossRef]

172. Shi, Y.; Zhang, B. Recent advances in transition metal phosphide nanomaterials: Synthesis and applications in hydrogen evolution reaction. Chem. Soc. Rev. 2016, 45, 1529–1541. [CrossRef]
178. Shang, Y.; Xu, X.; Gao, B.; Ren, Z. Thiomolybdate $[\text{Mo}_3\text{S}_3\text{S}_7]^2^-$ Nanoclusters Anchored on Reduced Graphene Oxide-Carbon Nanotube Aerogels for Efficient Electrocatalytic Hydrogen Evolution. *ACS Sustain. Chem. Eng.* 2017, 5, 8908–8917. [CrossRef]

179. Huang, Z.; Luo, W.; Ma, L.; Yu, M.; Ren, X.; He, M.; Polen, S.; Click, K.; Garrett, B.; Lu, J.; et al. Dimeric $[\text{Mo}_2\text{S}_3]^2^-$ Cluster: A Molecular Analogue of Mo$_2$S$_6$ Edges for Superior Hydrogen-Evolution Electrocatalysis. *Angew. Chem. Int. Ed.* 2015, 54, 15181–15185. [CrossRef]

180. Lei, Y.; Yang, M.; Hou, J.; Wang, F.; Cui, E.; Kong, C.; Min, S. Thiomolybdate $[\text{Mo}_3\text{S}_3\text{S}_7]^2^-$ nanocluster: A molecular mimic of Mo$_2$S$_6$ active sites for highly efficient photocatalytic hydrogen evolution. *Chem. Commun.* 2018, 54, 603–606. [CrossRef]

181. Kibsgaard, J.; Jaramillo, T.F. Molybdenum Phosphosulfide: An Active, Acid-Stable, Earth-Abundant Catalyst for the Hydrogen Evolution Reaction from Water. *Angew. Chem. Int. Ed.* 2013, 52, 10185–10189. [CrossRef]

182. Zhao, Y.; Kamiya, K.; Hashimoto, K.; Nakanishi, S. In Situ CO$_2$ Reduction with Platinum-Activated Multimetal Oxygen-Evolving Catalysts. *ChemSusChem* 2015, 8, 756–761. [CrossRef]

183. Gao, M.-R.; Liang, J.-X.; Zheng, Y.-R.; Xu, Y.-F.; Jiang, J.; Gao, Q.; Li, J.; Yu, S.-H. An efficient molybdenum disulfide/cobalt diselenide hybrid catalyst for electrochemical hydrogen evolution. *Nat. Commun.* 2015, 6, 5982. [CrossRef]

184. Tang, H.; Dou, K.; Kaun, C.-C.; Kuang, Q.; Yang, S. MoSe$_2$: A new efficient electrocatalyst for hydrogen production from water. *Energy Environ. Sci.* 2012, 5, 8912–8916. [CrossRef]

185. Puche, M.; Puche, M.; Atienzar, P.; Amor, J.; Cordier, S.; Molard, Y. In Situ Generation of Active Molybdenum Octahedral Clusters for Photocatalytic Hydrogen Production from Water. *ChemSusChem* 2016, 9, 1963–1971. [CrossRef] [PubMed]

186. Puche, M.; García-Abalo, R.; Mikhailyov, M.A.; Sokolov, M.N.; Atienzar, P.; Feliz, M.J.N. Enhanced Photocatalytic Activity and Stability in Hydrogen Evolution of Mo$_4$ Iodide Clusters Supported on Graphene Oxide. *Nanomaterials* 2020, 10, 1259. [CrossRef]

187. Vrubel, H.; Hu, X.; Béniac, A.; Gushchin, A.L.; Kozlova, E.A.; Laricheva, Y.A.; Abramov, P.A.; Sokolov, M.N.; Gómez, R.; Lana-Villarreal, T. Photogeneration of Hydrogen from Water by Hybrid Molybdenum Sulfide Clusters Immobilized on Titania. *ChemSusChem* 2015, 8, 148–157. [CrossRef]

188. Tran, P.D.; Nguyen, M.; Pramana, S.S.; Bhattacharjee, A.; Chiam, S.Y.; Fize, J.; Field, M.J.; Artero, V.; Loo, J.; et al. Copper molybdenum selenide: A new efficient electrocatalyst for hydrogen production from water. *Energy Environ. Sci.* 2012, 5, 8912–8916. [CrossRef]

189. Mohanty, B.; Ghorbani-Asl, M.; Kretschmer, S.; Ghosh, A.; Guha, P.; Panda, S.K.; Jena, B.; Krasheninnikov, A.V.; Jena, B.K. MoS$_2$ Quantum Dots as Efficient Catalysts for the Oxygen Evolution Reaction. *ACS Catal.* 2018, 8, 1683–1698. [CrossRef]

190. Hartley, C.L.; DiRisio, R.J.; Screen, M.E.; Mayer, K.J.; McNamara, W.R. Iron Polypyridyl Complexes for Photocatalytic Hydrogen Generation. *Inorg. Chem.* 2016, 55, 8865–8870. [CrossRef]

191. Jin, Y.; Wang, H.; Li, J.; Yue, X.; Han, Y.; Shen, P.K.; Cui, Y. Porous Mo$_2$S$_6$ Nanosheets as Non-noble Bifunctional Electrocatalysts for Overall Water Splitting. *Adv. Mat.* 2016, 28, 3785–3790. [CrossRef]

192. Kibsgaard, J.; Jaramillo, T.F. Molybdenum Phosphosulfide: An Active, Acid-Stable, Earth-Abundant Catalyst for the Hydrogen Evolution Reaction from Water. *Angew. Chem. Int. Ed.* 2012, 51, 14433–14437. [CrossRef]

193. Recatalá, D.; Llussar, R.; Gushchin, A.L.; Kozlova, E.A.; Laricheva, Y.A.; Abramov, P.A.; Sokolov, M.N.; Gómez, R.; Lana-Villarreal, T. Photogeneration of Hydrogen from Water by Hybrid Molybdenum Sulfide Clusters Immobilized on Titania. *ChemSusChem* 2015, 8, 148–157. [CrossRef]

194. Tran, P.D.; Nguyen, M.; Pramana, S.S.; Bhattacharjee, A.; Chiam, S.Y.; Fize, J.; Field, M.J.; Artero, V.; Loo, J.; et al. Copper molybdenum selenide: A new efficient electrocatalyst for hydrogen production from water. *Energy Environ. Sci.* 2012, 5, 8912–8916. [CrossRef]

195. Feliz, M.; Puche, M.; Atienzar, P.; Concepción, P.; Cordier, S.; Molard, Y. In Situ Generation of Active Molybdenum Octahedral Clusters for Photocatalytic Hydrogen Production from Water. *ChemSusChem* 2016, 9, 1963–1971. [CrossRef] [PubMed]

196. Chao, S.; Huang, J.; Wu, Y.; Shen, J.; Wang, H.; Yang, X.; Zhu, Y.; Li, C. Multimetalloc Ni–Mo/Cu nanowires as nonprecious and efficient full water splitting catalysts. *J. Mater. Chem. A* 2017, 5, 4207–4214. [CrossRef]

197. Tran, P.D.; Tran, T.V.; Orio, M.; Torelli, S.; Truong, Q.D.; Nayuki, K.; Sasaki, Y.; Chiam, S.Y.; Yi, R.; Honma, I.; et al. Coordination polymer structure and revisited hydrogen evolution catalytic mechanism for amorphous molybdenum sulfide. *Nat. Mat.* 2016, 15, 640–646. [CrossRef] [PubMed]

198. Mohanty, B.; Ghorbani-Asl, M.; Kretschmer, S.; Ghosh, A.; Guha, P.; Panda, S.K.; Jena, B.; Krasheninnikov, A.V.; Jena, B.K. MoS$_2$ Quantum Dots as Efficient Catalysts for the Oxygen Evolution Reaction. *ACS Catal.* 2018, 8, 1683–1698. [CrossRef]

199. Hartley, C.L.; DiRisio, R.J.; Screen, M.E.; Mayer, K.J.; McNamara, W.R. Iron Polypyridyl Complexes for Photocatalytic Hydrogen Generation. *Inorg. Chem.* 2016, 55, 8865–8870. [CrossRef] [PubMed]

200. Tran, P.D.; Tran, T.V.; Orio, M.; Torelli, S.; Truong, Q.D.; Nayuki, K.; Sasaki, Y.; Chiam, S.Y.; Yi, R.; Honma, I.; et al. Coordination polymer structure and revisited hydrogen evolution catalytic mechanism for amorphous molybdenum sulfide. *Nat. Mat.* 2016, 15, 640–646. [CrossRef] [PubMed]

201. Chao, S.; Huang, J.; Wu, Y.; Shen, J.; Wang, H.; Yang, X.; Zhu, Y.; Li, C. Multimetalloc Ni–Mo/Cu nanowires as nonprecious and efficient full water splitting catalysts. *J. Mater. Chem. A* 2017, 5, 4207–4214. [CrossRef] [PubMed]

202. Yang, Y.; Zhang, K.; Lin, H.; Li, X.; Chan, H.C.; Yang, L.; Gao, Q. Mo$_2$S$_6$–Ni$_3$S$_2$: Heteronanorods as Efficient and Stable Bifunctional Electrocatalysts for Overall Water Splitting. *ACS Catal.* 2017, 7, 2357–2366. [CrossRef]
204. Tang, Y.-J.; Liu, C.-H.; Huang, W.; Wang, X.-L.; Dong, L.-Z.; Li, S.-L.; Lan, Y.-Q. Bimetallic Carbides-Based Nanocomposite as Superior Electrocatalyst for Oxygen Evolution Reaction. *ACS Appl. Mater. Interfaces* 2017, 9, 16977–16985. [CrossRef]

205. Jin, Y.; Huang, S.; Yue, X.; Du, H.; Shen, P.K. Mo- and Fe-Modified Ni(OH)$_2$/NiOOH Nanosheets as Highly Active and Stable Electrocatalysts for Oxygen Evolution Reaction. *ACS Catal.* 2018, 8, 2359–2363. [CrossRef]

206. Li, Y.; Xu, H.; Huang, H.; Wang, C.; Gao, L.; Ma, T. One-dimensional MoO$_2$–Co$_2$Mo$_3$O$_8$@C nanorods: A novel and highly efficient oxygen evolution reaction catalyst derived from metal–organic framework composites. *Chem. Commun.* 2018, 54, 2739–2742. [CrossRef] [PubMed]

207. Yuan, Y.; Adimi, S.; Guo, X.; Thomas, T.; Zhu, Y.; Guo, H.; Priyanga, G.S.; Yoo, P.; Wang, J.; Chen, J.; et al. A Surface-Oxide-Rich Activation Layer (SOAL) on Ni$_2$Mo$_3$N for a Rapid and Durable Oxygen Evolution Reaction. *Angew. Chem. Int. Ed.* 2020, 59, 18036–18041. [CrossRef]

208. Shi, H.; Zhou, Y.-T.; Yao, R.-Q.; Wan, W.-B.; Ge, X.; Zhang, W.; Wen, Z.; Lang, X.-Y.; Zheng, W.-T.; Jiang, Q. Spontaneously separated intermetallic Co$_3$Mo from nanoporous copper as versatile electrocatalysts for highly efficient water splitting. *Nat. Commun.* 2020, 11, 2940. [CrossRef]