

Learning from Nature's Example: Repair Strategies in Light-Driven Catalysis

Alexander K. Mengele and Sven Rau*

Cite This: <https://doi.org/10.1021/jacsau.2c00507>

Read Online

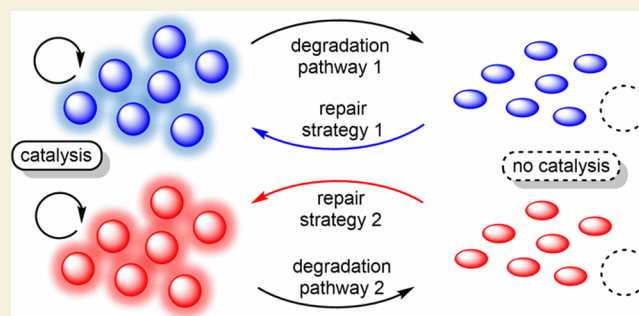
ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The continuous repair of subunits of the photosynthetic apparatus is a key factor determining the overall efficiency of biological photosynthesis. Recent concepts for repairing artificial photocatalysts and catalytically active materials within the realm of solar fuel formation show great potential in reshaping the research directions within this field. This perspective describes the latest advances, concepts, and mechanisms in the field of catalyst repair and catalyst self-healing and provides an outlook on which additional steps need to be taken to bring artificial photosynthetic systems closer to real-life applications.

KEYWORDS: photocatalysis, repair, healing, artificial photosynthesis, solar fuels



1. INTRODUCTION

Natural oxygenic photosynthesis that enabled the evolution of complex life on earth has likely started ca. 2.4 billion years ago.¹ The photosynthetic apparatus, i.e. the molecular machinery allowing the coupling of light absorption with water splitting and reductive assimilation of CO₂ leading to the formation of oxygen and organic matter, has attracted the interest of scientists for generations. The study of natural photosynthesis prompted scientists to rethink the future energy landscape in general^{2–4} and also fruitfully induced research in specific fields such as artificial photosynthesis^{5–7} or the development of bioinspired electrocatalysts.⁸

A functional analysis of the molecular photosynthetic apparatus leads to the conclusion that individual components of a man-made photocatalytic system should carry out individual tasks such as light-absorption-induced charge separation, electron transport, and catalytic turnover. In addition, nature also teaches mankind that even the most sophisticated systems might suffer from unavoidable degradation.⁹ Green plants have developed complex repair strategies to cope with the continuous degradation of vulnerable subunits critical to the functioning of the whole photosynthetic machinery (see Scheme 1).¹⁰ Consequently, the longevity of the photosynthetic apparatus in total is enhanced by molecular repair. Following the path outlined above of transferring concepts and lessons from nature to artificial systems as well as already promising examples of self-healing materials for e.g. water oxidation,¹¹ the next steps in improving many artificial (photo)catalytic systems is to better understand degradation

pathways¹² and consequently implement knowledge-guided repair and self-healing strategies.

Driven by the fact that natural photosynthesis has ever been a source for inspiration, the repair cycle of natural photosynthesis will be briefly outlined (see Scheme 1).^{9,10,13} The most vulnerable part of the photosynthetic apparatus is the D1 protein representing—along with the D2 protein—a core polypeptide structure within the reaction center of PSII (PS = photosystem). On illumination with high light intensity, the rate of the D1 replacement procedure can occur as often as twice per hour.¹⁰ Although the specific molecular processes ultimately triggering the photoinhibition of the photosynthesis via photodegradation of the D1 protein are still under debate ($\Phi \approx 10^{-7}$),⁹ the processes leading to the reactivation of the photosynthetic apparatus have been clarified to a large extent.¹³ When the D1 protein is damaged (step i in Scheme 1), phosphorylation induces the disassembly of PSII as well as the degradation of the no longer functioning D1 protein by different proteases (step ii). This process is followed by the *de novo* synthesis of the D1 protein and the reassembly of the functional PSII (step iii).¹³

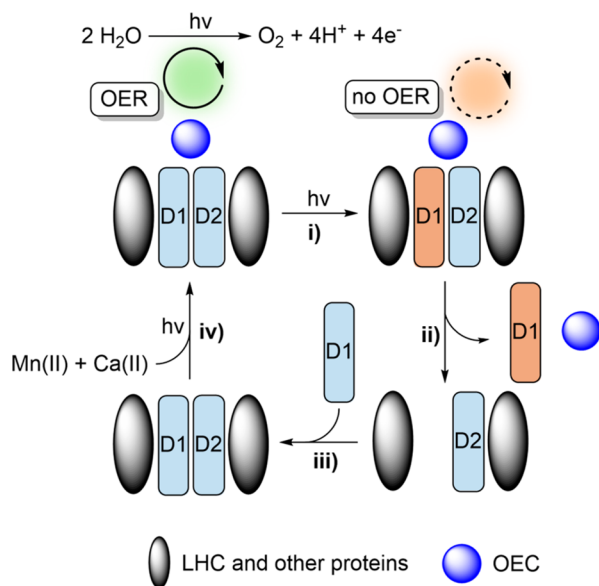
In contrast to degradation and resynthesis of the D1 protein, the final assembly step, i.e., the formation of the functional

Received: September 19, 2022

Revised: November 4, 2022

Accepted: November 10, 2022

Scheme 1. Simplified Scheme of Biological PSII Repair Representing the Elementary Steps of Photoinhibition by D1 Degradation (i), PSII Disassembly (ii), Implementation of *De Novo* Synthesized D1 (iii), and Photoinduced Reassembly of the OEC (iv)



oxygen-evolving complex (OEC) using Mn(II) and Ca(II) ions (step iv), is directly triggered by light. The stepwise assembly of the OEC is initiated by the PSII-mediated oxidation of Mn(II) to Mn(III), which initiates the coordination of further Mn(II) and Ca(II) ions, finally leading to the formation of the functional CaMn_4O_5 cluster. It can thus be stated that the repair of the natural photosynthetic apparatus exhibits both photoindependent and photodependent steps. As will be described below, both strategies have also been utilized for repairing artificial photosynthetic systems.

Concerning the terminology used within this article, it should be noted that self-healing is a specific type of repair defined as the *in situ* repair of the catalyst under operating

conditions without applying an additional external stimulus; for water-oxidizing catalysts self-healing has recently been extensively reviewed.¹¹ Following this systematic definition, all other systems that need some kind of external input (chemicals, light, etc.) under nonoperating conditions to induce the reactivation of catalytic activity do not exhibit self-healing properties and must be (actively, e.g. by human action) repaired. Finally, within this perspective the term repair (process) will be applied to all processes where a chemical reaction takes place that (i) regenerates the catalyst in its initial (or only a slightly altered) form and (ii) restores catalytic activity.

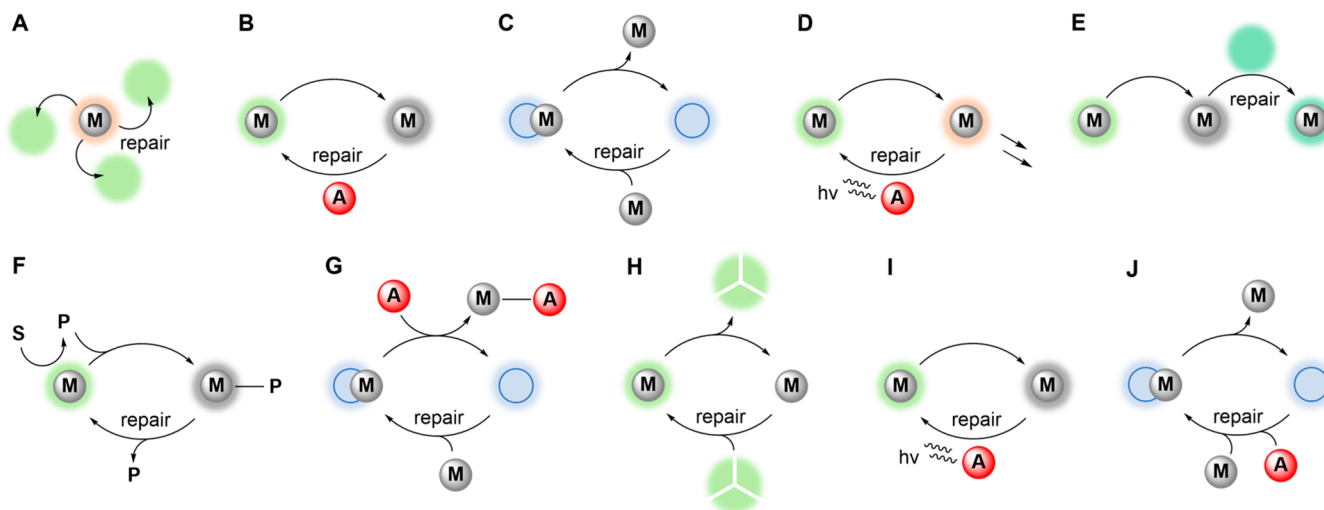
Rather than focusing on a specific field of catalyst repair, the goal of this perspective is to present the breadth of possible repair strategies in different areas: i.e., covering reductive as well as oxidative catalysis and treating both molecular systems and material-based catalysts, respectively. Although a variety of different mechanisms can lead to the loss of photocatalytic activity, these detrimental processes have been tackled so far by a limited number of concepts by which these degradation processes are reversed or ideally even inhibited (see Scheme 2). These concepts will be discussed in the following sections.

2. REPAIR CONCEPTS FOR MOLECULAR CATALYSTS

2.1. Concepts for Repairing the Loss of Structural Integrity of the Catalyst Unit Itself

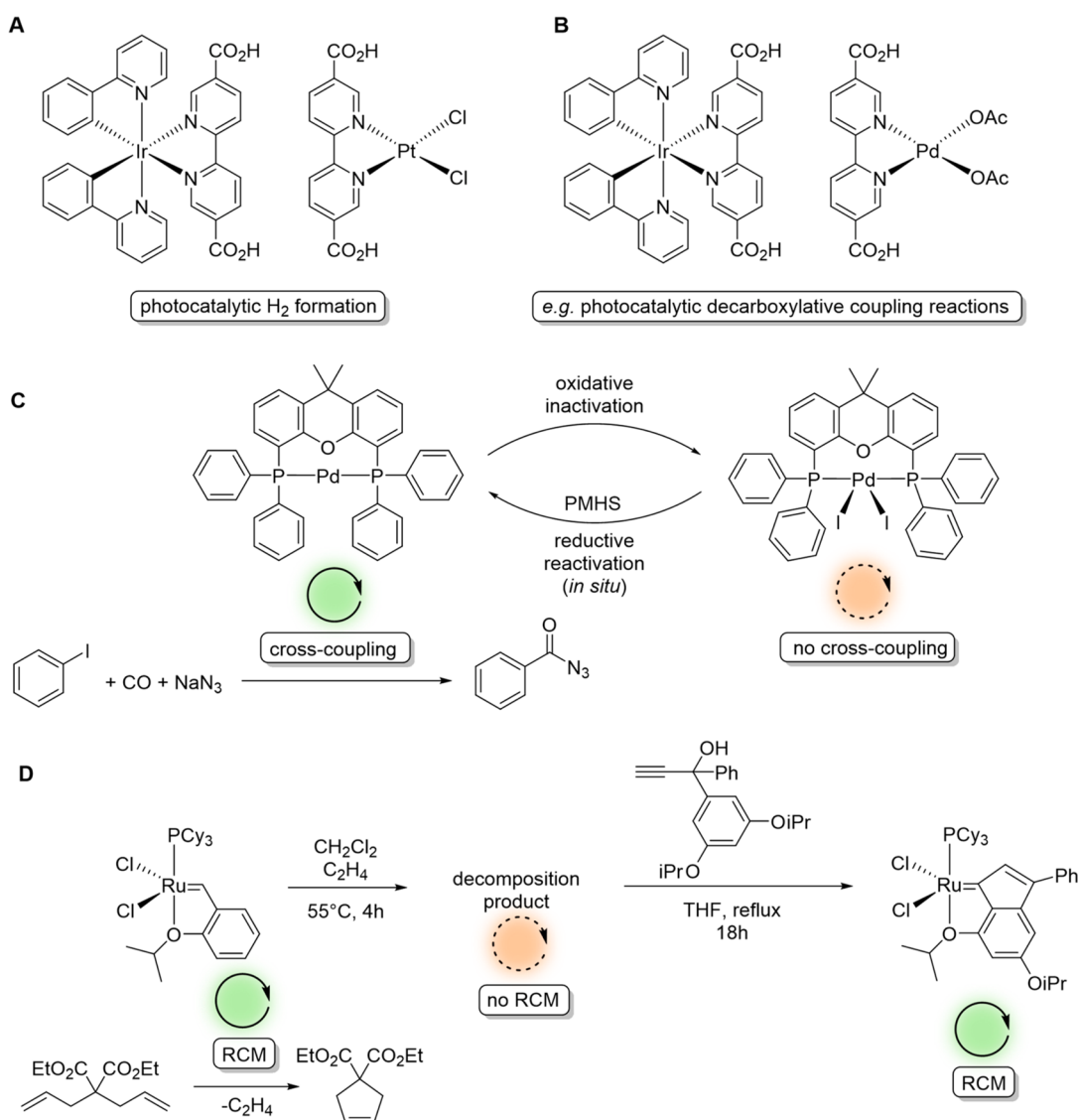
Light-driven hydrogen evolution using molecular artificial photosynthetic systems is regularly enabled using α -diimine complexes of simple Pt and Pd dihalides. The literature suggests that special requirements for the transition metal coordinating ligand sphere are necessary to avoid metal particle formation:¹⁴ i.e., by offering electron-withdrawing substituents or electron reservoir moieties.^{15–17} Recently another strategy has been reported how metal colloid formation can be inhibited: i.e., how fast self-healing, occurring at a higher rate than colloid formation, is achieved (Scheme 2A). The concept is based on metal–organic frameworks (MOFs), being built up by carboxylic acid functionalized bpy ligands (see Scheme 3A; bpy = 2,2'-bipyridine).¹⁸ The MOFs contain only a limited

Scheme 2. Pictorial Representation of Different Repair Strategies^a



^aGreen, orange, and gray represent stable, unstable, and inactivity-inducing ligand environments of metal catalyst M, respectively. Blue indicates a material capable of anchoring M, while reagents A are highlighted in red (S, substrate; P, product).

Scheme 3. Selection of Published Repair Strategies in the Realm of Molecular (Photo)catalysis: (A, B) Chromophore–Catalyst Pairs Which Are Attached to MOFs via Their CO₂H Groups;^{25,26} (C) Reductive *In Situ* Repair of [(xantphos)Pd];²⁷ (D) Repair of a RCM Ru Catalyst²⁸



number of [(ppy)₂Ir(bpy)]⁺ chromophores (ppy = 2-phenylpyridine) and [(bpy)PtCl₂] catalysts as well as a varying amount of vacant α -diimine binding sites. In presence of an 100-fold excess of vacant bpy moieties, the MOF did not show any signs of colloid formation. In contrast, a lower bpy excess leads to slow particle formation. Interestingly, the duration of molecular catalysis was also prolonged when an excess of free bpy ligand was added to the MOF-free homogeneous reference catalysis solution. However, the longevity-boosting effect was not as pronounced as for the MOF itself, where intermediately decoordinated Pt centers are more efficiently recaptured by the directly available α -diimine sites. This is enabled by their higher local concentration in the MOF architecture and the concomitantly constrained movement of the coordinatively labile Pt moieties. This strategy represents a very promising concept and should consequently be pursued further.

This is also highlighted by another report where the self-healing strategy by offering vacant α -diimine sites (Scheme 2A) has recently been utilized for the recycling of very similar MOFs bearing MOF-linked [Ru(bpy)₃]²⁺ chromophores and

the same [(bpy)PtCl₂]-based catalysts as described above.¹⁹ The recycled material did not show any signs of degradation for three consecutive runs of light-driven hydrogen evolution.

The self-healing concept for prolonging molecular catalysis by recoordination of labile metal centers via addition of excess ligand (Scheme 2A) has also been investigated in the area of [CoCl(dmgh)₂(py)] complexes (dmgh₂ = dimethylglyoxime; py = pyridine). When this Co catalyst and eosin Y were combined in the presence of triethanolamine (TEOA, an electron donor), light-driven hydrogen evolution was observed.²⁰ The longevity of the photocatalytic system as well as the finally obtained turnover number (TON) could be increased stepwise by addition of 6 and 12 equiv of free dmgh₂, respectively. In the latter case and based on the amount of utilized Co catalyst, a TON of 900 was obtained. In a follow-up publication Eisenberg and co-workers reported two further details: ligand exchanges (of py and dmgh) at the Co center are drastically increased when Co(III) (a d⁶ system) is reduced to coordinatively more labile Co(II) (a d⁷ system), e.g. under photoreductive conditions, and after reaching

complete inactivity a repair process can be performed.²¹ This process is based on the hypothesis that during reductive photocatalysis the dmgH_2 ligand became hydrogenated or decomposed otherwise so that the active Co(I) state can no longer be thermodynamically accessed using eosin Y as a chromophore. Exploiting the reduction-induced fast ligand exchange at the Co catalyst thus opens the possibility that the addition of fresh dmgH_2 reactivates the catalytic system by replacing the hydrogenated bidentate ligand from the Co center (Scheme 2B; A = reduction equivalents). The repair concept of photochemistry-induced ligand exchanges via a light-driven variation of the metal's redox state in the inactive decomposition product is thus a very elegant way to repair catalysts that do not suffer from metal–ligand bond dissociation loss but from disadvantageous ligand transformations.

In addition to the dynamic coordination chemistry of Co centers and dmgH_2 ligands, also Co-N_{py} bonds were utilized as repair sites for light-driven hydrogen evolution. In a MOF equipped with a $[\text{CoCl}(\text{dmgH})_2(\text{py})]$ -like complex where the py ligand is covalently connected to the MOF skeleton, light-driven H_2 formation of the functionalized MOF using eosin Y as a freely diffusing chromophore is accompanied by 90% Co loss after 20 h of irradiation (TON = 45 per Co center).²² However, the system could be repaired by linking new Co centers to the py moiety of the MOF via *post mortem* treatment with $[\text{CoCl}_2(\text{dmgH})(\text{dmgH}_2)]$ (Scheme 2C). By this, 60% of the initial activity could be restored. Furthermore, as the catalytic activity of the MOF-based photocatalytic system was notably higher than that of the homogeneous reference system, the authors concluded that the porous structure of the MOF partially inhibited leaching of the Co centers during catalysis, thus keeping them in close proximity to the unbound py ligands and consequently facilitating self-healing via recoordination. It should also be noted that in a heterodinuclear Fe–Co photocatalyst the light-independent dissociation of the Co center from the N_{py} atom occurred by simply diluting the catalyst in acetonitrile (MeCN).²³ In such cases, recoordination-driven self-healing of the dinuclear species, i.e. the active catalyst, might only take place efficiently at high concentration. Finally, it should be mentioned that a hybrid system consisting of photosystem I (PSI) and $[\text{CoCl}(\text{dmgH})_2(\text{py})]$ yielded ca. 5200 molecules of H_2 per PSI. Efforts to restore photocatalytic activity via addition of fresh $[\text{CoCl}(\text{dmgH})_2(\text{py})]$ have so far been unsuccessful.²⁴

Pd-based systems have been shown to exhibit an even higher tendency to form metal particles than their Pt congeners, as evident from studies on, e.g., heterodinuclear Ru–BL–Pd complexes (BL = bridging ligand).^{17,29} Low-valent Pd species, which disadvantageously also tend to aggregate to metal clusters, are important intermediates in oxidative organic transformations as well, such as decarboxylative coupling of allylic alcohols or C–H alkenylation of 2-phenyl phenols. Jiang and co-workers developed bifunctional photocatalytically active MOFs based on carboxylic acid functionalized $[(\text{ppy})_2\text{Ir}(\text{bpy})]^+$ chromophores and $[(\text{bpy})\text{PdX}_2]$ catalysts (X = OAc, TFA (=trifluoroacetate); see Scheme 3B) for the organic transformations named above.²⁶ By illuminating the MOF samples during oxidative organic transformations, the Pd colloid formation was suppressed, and a strongly enhanced activity (25-fold compared to the homogeneous reference system) of the MOF material for the photooxidative substrate transformations was observed. This effect was ascribed to the

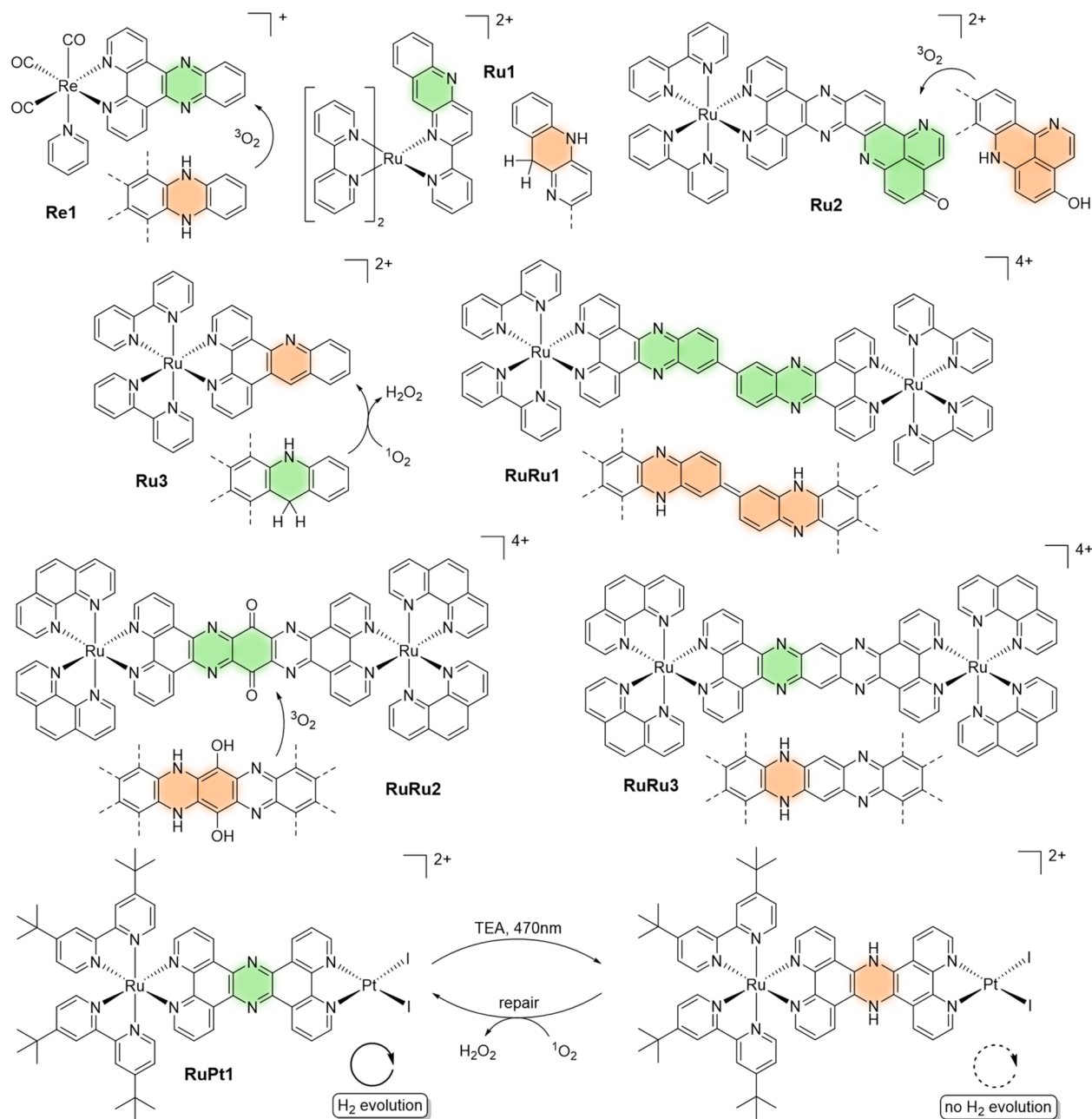
efficient reoxidation of Pd(0) centers by electron transfer to nearby photoexcited Ir centers; oxygen serves as a terminal electron acceptor (Scheme 2D).

However, Pd-based catalysts for hydrogen formation tend to be more active than the related Pt analogues. It is therefore very relevant to investigate strategies which may lead to the stabilization of the Pd metal to ligand bond in all oxidation states of the metal center. Here, organometallic catalysis has developed some very interesting concepts. For the Pd-catalyzed azidocarbonylation of aryl iodides Grushin and colleagues have reported a repair process.²⁷ In contrast to the aforementioned MOF system, the catalytically active species is a robustly phosphine bound Pd(0) center, and the poisoned catalyst was identified as $[(\text{xantphos})\text{PdI}_2]$. Based on the identification of the degradation product, a continuous repair process was developed (see Scheme 3C). The catalytic activity of the Pd-catalyzed cross-coupling reaction can be increased by addition of PMHS (polymethylhydrosiloxane), which reliably re-forms xantphos-stabilized Pd(0) from intermittently generated and catalytically inactive $[(\text{xantphos})\text{PdI}_2]$ (Scheme 2B; A = PMHS). In the future this successful redox-chemistry-based repair strategy may also be applied to other systems. If the degradation products have been identified as structurally intact systems not being capable of returning back into the catalytic cycle due to the lack of energetically suitable redox equivalents, repair by suitable oxidants or reductants represents a viable option in reviving catalytic activity.

For the ring-closing metathesis (RCM) reaction of diallylmalonate using the first-generation Hoveyda–Grubbs catalyst a repair process has been developed as well.²⁸ To study the repair of one of the most likely occurring catalyst degradation products, the first-generation Hoveyda–Grubbs catalyst was purposely inactivated with ethylene (see Scheme 3D). After analyzing the chemistry of this intermediate, treatment of the Ru-based decomposition product from RCM with 1-(3,5-diisopropoxy-phenyl)-1-phenylprop-2-yn-1-ol for 18 h in THF under reflux resulted in the reactivation of only 43% of the initially employed Ru catalyst (Scheme 2E). However, RCM still proceeded with 90% yield when the repaired system was allowed to react for longer times.

A detailed study into the light-driven formation of CO from CO_2 offers an insight into another important aspect limiting catalytic activity. A simple repair/recycling process has been described for the photocatalytic CO_2 reduction to CO using $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Co}(\text{bpy})_3]^{3+}$ complexes as chromophores as well as catalysts, respectively.³⁰ Irrespective of the linkage of $[\text{Ru}(\text{bpy})_3]^{2+}$ to a Nafion membrane, a simple restoration of catalytic activity was obtained by thoroughly degassing the catalytic solution with fresh CO_2 (Scheme 2F). The loss of catalytic activity after several hours of CO formation was assigned to poisoning of the Co catalyst by the diatomic product. Additionally, product trapping within polymer pores is a well-known effect.⁵¹ Although no specific information on the binding parameters for these Co catalysts and CO or CO_2 were given for the $[\text{Co}(\text{bpy})_3]^{3+}$ -containing system, an analysis of similar Co-based CO_2 reducing catalysts containing macrocyclic N-donor ligands revealed that CO binds to Co(I) centers ca. 10^4 times stronger than CO_2 does.³² Although the authors claim that CO is removed efficiently from the Co center in the presence of excess CO_2 , thus allowing the simple recovery of catalytic activity, an analysis of the binding constants from related Co catalysts suggests that significantly more CO_2 will have to be utilized for catalyst

Scheme 4. Ligand Hydrogenation Processes Taking Place from Green to Orange as well as Reported Oxygen-Dependent Reoxidation Processes of Different Transition Metal Complexes^{41–49,51}



regeneration than the amount that has catalytically been converted (TON < 10). If the excess CO₂ utilized for this repair process would not be used for any further processes, this repair strategy would likely have to be seen to be critical from an environmental point of view. A similar effect was also observed for a Ni cyclam complex showing CO₂ reducing electrocatalytic activity. Only upon addition of a suitable CO scavenger is the catalyst efficiently freed from strongly bound CO and the electrocatalytic activity is increased by a factor of 10 (Scheme 2F).³³

Following the route depicted in Scheme 2C, repair of a hydrogen-bonded organic framework containing [(bpy)Re(CO)₃Cl] sites for the light-driven reduction of CO₂ has been recently reported as well.³⁴ After eight cycles, the drop of the material's catalytic activity to ca. 50% of its

initial value is assigned to Re leaching. Postfunctionalization of the material collected after eight cycles with fresh Re moieties lead to a return of its initial catalytic performance. Especially if less costly transition-metal catalysts would be utilized, these remetallation processes of sophisticated substrates (Scheme 2C) could become cost-efficient repair processes.

Mechanistically connected to these processes is a 2,2':6',2''-terpyridine (tpy)-functionalized polymer, in which the programmed assembly and disassembly with tpy-substituted [Ru(bpy)₃]²⁺ complexes was investigated. Mg²⁺-induced assembly of polymer and Ru complex via a [(tpy)Mg(tpy)]²⁺ motif is associated with increased photo(electro)chemical activity: e.g., photooxidative dimerization of benzylamine.³⁵ Programmed disassembly—and accordingly a decrease in photocatalytic activity—is observed when TBAF as a fluoride

source is added due to the formation of MgF_2 . The Ru-functionalized polymer can be repaired after a washing step when fresh tpy-functionalized $[\text{Ru}(\text{bpy})_3]^{2+}$ complex and Mg^{2+} ions are added to the solution.

A similar “disassembly and repair on purpose” process, typically employed to induce a specific catalyst deactivation process and probe repair strategies for the selected degradation pathway, has been described by Streb and colleagues (Scheme 2G; A = ethylenediaminetetraacetic acid (EDTA)).³⁶ The Cu-functionalized polyoxovanadate $\{\text{CuV}_{12}\}$ was utilized for the oxidation of 1-phenylethanol to acetophenone using *tert*-butyl hydroperoxide (*t*BuOOH) as oxidant. Addition of EDTA led to an immediate stop of alcohol oxidation by removing Cu(II) from the polyoxometalate (POM) scaffold via precipitation of a Cu-EDTA complex. Targeted repair of the active catalyst is possible by addition of fresh $\text{Cu}(\text{NO}_3)_2$. The efficient remetallation of the polyoxovanadate $\{\text{V}_{12}\}$ under catalytic conditions was also confirmed by mixing it with $\text{Cu}(\text{NO}_3)_2$ at the start of the catalytic process and observing activity identical to that for the independently synthesized $\{\text{CuV}_{12}\}$. This indicates that in a mixture of Cu(II) ions and the POM $\{\text{V}_{12}\}$ the active catalyst $\{\text{CuV}_{12}\}$ represents the thermodynamically most stable species.

The property of POM-based systems, i.e., the catalytically active state represents at the same time the thermodynamic sink of the system, even under catalytic conditions, has also been exploited by other groups. In fact, these characteristics would qualify a catalyst to be active indefinitely, even if it equilibrates to a certain extent into smaller (sub)structures during catalytic operation (Scheme 2H).³⁷ Therefore, this self-healing-based longevity and the possibility to self-assemble from simple inorganic precursor salts rendering the presynthesis of the catalyst unnecessary make these POM catalysts highly attractive for industrial applications. The proposed self-assembly of active POMs during catalysis from simple inorganic salts has been utilized not only for their application in the selective epoxidation of *cis*-stilbene³⁸ but also for the oxidation of lignin into CO_2 and H_2O ³⁹ as well as the oxidation of alcohols to the corresponding aldehydes, ketones, and carboxylic acids in the presence of H_2O_2 .⁴⁰

2.2. Reversal of Ligand Hydrogenations As Repair Strategy for Structurally Stable Photocatalysts

In the previous section many repair strategies were based on reestablishing the direct chemical environment of the catalytically active center (i.e., the first coordination sphere), which has been altered in the course of catalysis. Although to some extent intertwined (see the exploitation of dmgH_2 ligand exchange reactions for the repair of $[\text{CoCl}(\text{dmgH})_2(\text{py})]$), the often occurring ligand hydrogenation processes and their impact on ceasing catalytic activity as well as opening possibilities for molecular repair will be discussed in the following paragraphs.

Under the conditions necessary for reductive photocatalysis, π -extended aromatic ligand scaffolds containing N or other heteroatoms are prone to ligand hydrogenation^{41–51} by two or more sequential reduction and protonation events or by a reaction cascade involving a proton-coupled electron transfer (PCET), followed by the disproportionation of two semi-hydrogenated species.^{44,46} In contrast to all other complexes shown in Scheme 4, **RuRu2** is the only system capable of not only storing two but rather four redox equivalents on its central BL.⁴¹ These ligand hydrogenation processes have mainly been

investigated for $[\text{Ru}(\text{bpy})_3]^{2+}$ -like systems (see Scheme 4) and are known to alter the photophysical properties of the complexes, sometimes even dramatically.^{42,48} For example, the photochemical reduction of $[\text{Ru}(\text{bpy})_2(\text{bpp})]^{2+}$ (**Ru3** in Scheme 4) by two electrons led to the formation of an NADH-like bppH_2 ligand (bpp = benzo[*b*]pyrido[3,2-*f*][1,7]-phenanthroline). This diminished the luminescence quantum yield of the complex by more than 60%.⁴⁸ Complete loss of luminescence upon formation of the hydrogenated state was observed for **RuRu1** by offering a ligand-centered low-lying π - π^* state.⁴² Very active and stable intramolecular photocatalysts for H_2 generation suffer from a related deactivation pathway. For $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{PtI}_2](\text{PF}_6)_2$ (**RuPt1** in Scheme 4) a gradual decrease of photocatalytic hydrogen evolution activity can be associated with the slow *in operando* formation of the tpphz-hydrogenated species (tbbpy = 4,4'-*tert*-butyl-2,2'-bipyridine, tpphz = tetrapyridophenazine).⁵¹ Light-driven hydrogenation of the phenazine moiety of the corresponding mononuclear Ru complex has previously been described as well.⁵⁰

The technically simple reoxidation of different hydrogenated Ru complexes by reeration of the solutions or *in situ* formation of $^1\text{O}_2$ (see Scheme 4) allowed the development of an active repair cycle for **RuPt1**.⁵¹ It should be noted that the use of either $^3\text{O}_2$ (Scheme 2B; A = $^3\text{O}_2$) or $^1\text{O}_2$ (Scheme 2I; A = $^1\text{O}_2$ generated by a Ru complex) is associated with the fact that different hydrogenated ligand spheres exhibit varying reactivities resulting from their different thermodynamic stabilities.⁵² For rather stable systems such as **Ru3** and **RuPt1**, an efficient repair process is only possible upon light-driven formation of more reactive $^1\text{O}_2$ ($E(^1\text{O}_2/\text{O}_2^{\bullet-}) = +1.07$ V vs NHE and $E(^3\text{O}_2/\text{O}_2^{\bullet-}) = +0.10$ V vs NHE).⁵³

Consequently, after a plateau for light-driven H_2 formation by **RuPt1** had been reached, evaporation of the solvent mixture used for photocatalysis (MeCN:TEA: H_2O = 6:3:1, v:v:v) and subsequent addition of fresh, air-equilibrated MeCN along with irradiation of the MeCN solution of hydrogenated **RuPt1** for several minutes led to the regeneration of the active catalyst and H_2O_2 as a byproduct (Scheme 2I; note that concomitant **RuPt1** reduction as well as TEA oxidation by $^1\text{O}_2$ prevents the light-driven repair process of hydrogenated **RuPt1** in the solvent mixture used for photocatalysis). By repeating these processes at the end of each photocatalytic run, the 8-fold recycling of **RuPt1** led to an increase of the total turnover number (TON) by a factor of ca. 7, reaching values of more than 3000. This highlights that the search for reasonable repair strategies is very important for increasing the catalytic output per molecule and consequently improving the cost efficiency of photocatalytic H_2 evolution.⁵⁴ Interestingly, **RuPt1** can also be repaired by adding excess $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to the catalytic solution after hydrogen formation has stopped (Scheme 2B, A = $(\text{NH}_4)_2\text{S}_2\text{O}_8$).⁵¹

3. REPAIR AND SELF-HEALING OF CATALYTICALLY ACTIVE MATERIALS

A large number of materials used for the (photo)-electrocatalytic splitting of water (mainly water oxidation) exhibit self-healing properties as defined by Thorarinsdottir et al.:¹¹ i.e., without any human intervention the catalytically active species reestablishes itself under the operating conditions. These catalysts thus possess theoretical immortality when brought into the correct chemical environment.

Before discussing self-healing oxygen evolution catalysts, other material-applied repair strategies are described. Similar to the oxygen-driven reversal of ligand hydrogenation in Ru complexes—including hydrogen evolving photocatalyst **RuPt1**⁵¹—the material SION-X, i.e. $\text{Cu}_2[(\text{BO})(\text{OH})_2](\text{OH})_3$, can also be regenerated after quantitative catalytic H_2 release from ammonia–borane to its initial chemical composition via simple re-aeration of the reaction mixture (Scheme 2B; $A = {}^3\text{O}_2$).⁵⁵ By that, the intermediately formed and catalytically active Cu(0) nanoparticles (NPs) are converted to Cu(II), leading to the regeneration of SION-X. This repair procedure could be repeated for 50 cycles without significant loss of Cu.

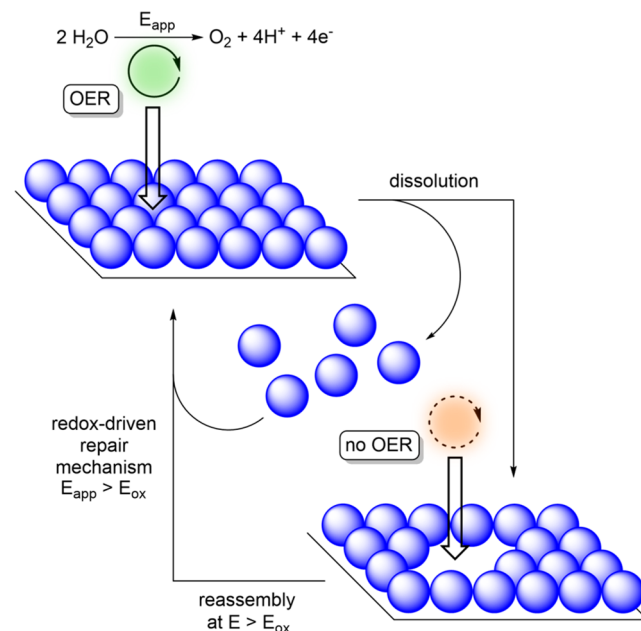
Another unique repair strategy was reported for an α -FeOOH@g-C₃N₄ catalyst utilized for the radical-driven degradation of bisphenol A.⁵⁶ The latter is decomposed by an Fe(II)-consuming reductive radical formation of persulfate. The continuous *in situ* “healing process” of the Fe centers is based on the light-driven reduction of Fe(III) to Fe(II) by g-C₃N₄ (Scheme 2I). As Fe leaching from the visible-light-absorbing g-C₃N₄ was low, recycling of the hybrid material and its use for several bisphenol A degradation runs could be demonstrated.

Although the vast majority of self-healing materials have been reported for the water oxidation reaction (see below), these interesting properties have also been identified in a system utilized for the photoelectrochemical hydrogen formation.⁵⁷ 2D WSe₂ was used as a substrate for film-forming $\text{Mo}_n\text{O}_x\text{S}_y$ complexes. The combination of efficient hydrogen evolution as well as point defect covering was ascribed to a multicomponent behavior of various mono-, di-, and trimeric Mo complexes (Scheme 2C). Whereas some of the catalytically less active complexes showed a high tendency for adsorption on 2D WSe₂ at point defects formed during catalysis, other Mo complexes being part of the film represented efficient hydrogen-evolving catalysts.

Self-healing properties were also observed in Co₃O₄ nanorods (NRs) used for the Fischer–Tropsch synthesis (FTS) of hydrocarbons.⁵⁸ During FTS in the presence of water CoOOH species are formed on the material's surface. In contrast to also investigated Co₃O₄ NPs, where an ever-increasing CoOOH peak was found by Raman spectroscopy during FTS, Co₃N₄ NRs exhibited limited and even reversible CoOOH formation. The mechanism behind the reversibility of CoOOH poisoning on Co₃O₄ NRs is the exergonic reduction of Co³⁺ centers to Co(0) at the NR surface (Scheme 2B; $A = \text{H}_2$). Due to the fact that the NPs exhibit Co²⁺ centers on their surface as a consequence of another crystal facet pointing toward the surrounding medium as well as the endergonic formation of metallic Co(0) from these Co²⁺ centers, no self-healing properties were observed for Co₃O₄ NPs. As this crystal-facet-dependent effect is very prominent, self-healing induced by surface engineering might be another highly relevant aspect of future catalyst studies.

After highlighting some currently unique repair and self-healing properties of selected materials, the much more thoroughly investigated Co-, Ni-, and Mn-oxide systems for the (photo)electrochemical oxygen evolution reaction (OER) will be described in the following text.^{11,13} Although each of these systems has its own characteristics regarding the specific molecular steps involved in OER and self-healing, they all follow the very simplistic global steps depicted in Schemes 5 and 2J ($A =$ oxidation equivalents at the electrode surface).¹¹ As a consequence of the different redox states of the metal

Scheme 5. Schematic Representation of Catalytically Active Materials for Water Oxidation and Their *In Situ* Repair by Redox-Chemistry-Driven Self-Healing



centers inevitably being part of the catalytic cycle of OER as well as the metals' redox-state-dependent solubilities and dissolution rates, the breakup of the catalyst film via loss of reduced metal centers into the surrounding medium is observed. However, if reoxidation of the dissolved metal centers occurs at a lower anodic potential than the potential needed for performing OER and the rate of reassembly is equal to or larger than the rate of catalyst dissolution, self-healing of the OEC utilizing the dissolved metal ions can occur. Interestingly, the assembly of the natural blueprint, i.e. the OEC of PSII, occurs in a similar fashion.¹³ As described above, the high redox potential of PSII is utilized to (photo)oxidize Mn(II) to Mn(III), initiating the metal oxide cluster formation (see step iv in Scheme 1).

For the Co-based systems atomistic insights into their working principle have been obtained.^{11,59–62} These self-healing Co catalysts are obtained as thin films via anodization of dilute Co²⁺ solutions containing suitable counterions such as phosphate, methylphosphonate, or borate (CoP_i, CoMeP_i and CoB_i catalysts).^{63,64} For CoP_i the role of phosphate is (i) to prohibit the formation of giant three-dimensional Co-oxide domains (typical cobaltate clusters consist of 10–60 Co centers)^{11,65} via surface capping that blocks further cluster growth and (ii) to serve as a basic acceptor of those protons being released during the OER.¹¹ The Co:P ratio is ca. 2:1.⁶³ In neutral and only slightly basic solutions and in the absence of suitable proton-accepting electrolytes, the metal oxide itself would serve as the most basic sites in the reaction mixture, resulting in protonation-induced catalyst film dissolution.^{11,61}

During the OER the octahedrally oxo-surrounded Co centers exist as Co²⁺, Co³⁺ (resting state), and Co⁴⁺.^{11,59,61,62} During the final reductive elimination step of the O₂ molecule from the actual catalytically active Co₂ edge sites of the cobaltate clusters,⁶⁰ Co²⁺ centers are formed. Co²⁺ exhibits a d⁷ electron configuration and consequently monoelectronic population of the antibonding e_g* orbital in an octahedral ligand environment is associated with these Co²⁺ centers being

prone to ligand exchange and dissolution (replacement of bridging oxides or hydroxides in the solid vs water) if not rapidly reoxidized to Co^{3+} .¹¹

Self-healing of the active CoP_i film occurs via reassembly of the dissolved $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ ions by a disproportionation process.¹¹ At the applied potential (E_{app}) for the OER a significant amount of $\text{Co}(\text{IV})$ centers is present in the catalyst film. The presence of $\text{Co}(\text{IV})$ centers at potentials 0.2 V lower than E_{app} represents the actual “trick” of CoP_i self-healing as reassembly of Co^{2+} ions from solution results in the formation of two substitutionally inert Co^{3+} centers.

Due to its remarkable self-healing properties under neutral conditions and ion-containing water, the CoP_i -based water oxidation has been interfered with several biological systems. The OER provided electrons not only for the CoP -catalyzed formation of H_2 which later was consumed by *Ralstonia eutropha* for CO_2 assimilation yielding biomass and fusel alcohols⁵ but also for the ambient N_2 fixation using *Xanthobacter autotrophicus*.⁶ This solar-powered nitrogen fixation process served as a fertilizing system for the improved growth of radishes.

In contrast to the Co-based catalysts which typically show self-healing at pH values greater than 5.2, the related Mn-OECs are self-healing even in a very acidic environment (up to pH = -0.5). Catalyst dissolution likely occurs via high-spin d^5 Mn(II) centers, but reoxidation to Mn(IV) again occurs at potentials lower than that used for OER.⁶⁶ NiB_i systems have also been reported as self-healing OER catalysts between pH 9 and 14.⁶⁷ They outperform CoP_i -OECs at basic pH, but CoP_i remains the superior catalyst under neutral conditions.

Finally, in contrast to these monometallic systems described above, mixed-metal oxide OECs have been investigated as well. The idea behind these mixed systems is that either a structurally robust metal oxide is combined with a catalytically highly active species leading to both high activity and high stability⁶⁸ or that several catalytically active centers beneficially influence each other.¹¹ High robustness for OER has, for example, been shown in the case of NiFeO_x films deposited from 2 M carbonate solutions⁶⁹ and NiCoFe-B_i systems⁷⁰ as well as NiFe -OECs assembled on BiVO_4 , where self-healing was assigned to site-specific redeposition of the active NiFe catalyst at point defects on bare BiVO_4 .⁷¹

4. CONCLUDING REMARKS

Various strategies for the repair of molecular- as well as material-based catalysts have been highlighted. In order to design rational repair and healing processes or even a complete inhibition of catalyst degradation for a specific catalytic system, the identification of the molecular processes leading to ceasing of catalytic turnover is necessary. The currently most advanced systems exhibit autonomous additive-free self-healing properties. This is due to the fact that under operating conditions the thermodynamically most stable configuration of the systems represents at the same time the active catalyst. On the molecular level this is true for different POM-based catalysts utilized for various oxidation reactions,^{37–40} whereas on the material level a larger number of self-healing systems are known: i.e., $\text{Mo}_x\text{O}_x\text{S}_y$ -based catalysts for photoelectrochemical hydrogen evolution,⁵⁷ Co_3O_4 NRs for FTS,⁵⁸ and various (mixed) metal oxides serving as electrocatalysts for water oxidation under different conditions.¹¹ However, also in the case of systems where human intervention is necessary to restart catalysis, i.e., a stimuli-induced active repair process has

to be performed to temporarily alter the conditions to which the catalyst is exposed, potentials are far from being exhausted. For such systems where the thermodynamics prohibit continuous *in operando* self-healing and limited longevity is only obtained by kinetic stabilization of the catalytically active configuration, technically simple and economically viable repair strategies can represent solutions for the problem of gradual catalyst degradation.

Therefore, further research on rational repair and healing strategies is highly recommended; as technically feasible repair processes offer the reactivation of the catalyst and its use for a second, third, fourth, and *n*th run, it will save precious resources. Only if the development of straightforward repair processes or self-healing (molecular) artificial photosynthetic schemes is successful will these systems come closer to their urgently needed real-life applications.

Promising strategies to also bring systems other than the self-healing water oxidizing catalysts closer to everyday life applications are, for example, the research on POMs to discover further molecular metal oxides combining high catalytic activity and the intriguing property that the catalytically active species represents the structural thermodynamic sink of the system. Furthermore, also the design of sophisticated but chemically stable substrates offering catalytic-activity-boosting binding sites for cost-efficient metal centers is highly interesting as well. The repair has been shown to proceed efficiently via remetallation in many systems. Also, the application of cheap oxidants or reductants to catalytic mixtures seems to be an important aspect for further developments in the field. As shown for e.g. the CoP_i system (Scheme 5), RuPt1 (Scheme 4) or $[\text{xantphos}]\text{Pd}$ (Scheme 3), (*in situ*) redox-chemistry-driven reintegration of the deactivated species into the catalytic cycle had a tremendous effect on the overall obtained catalytic output. To come closer to real-life applications it is a fact that, as in natural photosynthesis, also artificial systems need to have integrated repair or self-healing concepts that deal with the omnipresent redox changes during water oxidation/reduction and the associated instability/deactivation problems resulting thereof. Structurally simple or chemically robust catalysts may assist this development by limiting the number of possible degradation products that need to be considered in the design of suitable repair/self-healing strategies.

AUTHOR INFORMATION

Corresponding Author

Sven Rau – Institute of Inorganic Chemistry I, Ulm University, 89081 Ulm, Germany; orcid.org/0000-0001-9635-6009; Email: sven.rau@uni-ulm.de

Author

Alexander K. Mengele – Institute of Inorganic Chemistry I, Ulm University, 89081 Ulm, Germany; orcid.org/0000-0001-6496-3429

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacsau.2c00507>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: Alexander Klaus Mengele project administration, writing-original draft, writing-review & editing;

Sven Rau conceptualization, funding acquisition, project administration, resources, supervision, writing-review & editing.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)–Projektnummer 364549901, TRR 234 [A1]–is gratefully acknowledged.

ABBREVIATIONS

BL, bridging ligand; bpp, benzo[*b*]pyrido[3,2-*f*][1,7]-phenanthroline; bpy, 2,2'-bipyridine; dmgH₂, dimethylglyoxime; EDTA, ethylenediaminetetraacetic acid; FTS, Fischer–Tropsch synthesis; MeCN, acetonitrile; MOF, metal–organic framework; NP, nanoparticle; NR, nanorod; OEC, oxygen-evolving complex; OER, oxygen evolution reaction; PCET, proton-coupled electron transfer; PMHS, polymethylhydrosiloxane; POM, polyoxometalate; PS, photosystem; ppy, 2-phenylpyridine; py, pyridine; RCM, ring-closing metathesis; tbbpy, 4,4'-*tert*-butyl-2,2'-bipyridine; *t*BuOOH, *tert*-butyl hydroperoxide; TEOA, triethanolamine; TON, turnover number; tpphz, tetrapyridophenazine; tpy = 2,2':6', 2''-terpyridine.

REFERENCES

- (1) Fischer, W. W.; Hemp, J.; Johnson, J. E. Evolution of Oxygenic Photosynthesis. *Annu. Rev. Earth Planet. Sci.* **2016**, *44*, 647–683.
- (2) Armaroli, N.; Balzani, V. The Future of Energy Supply: Challenges and Opportunities. *Angew. Chem. Int. Ed* **2007**, *46* (1–2), 52–66.
- (3) Nocera, D. G. The Artificial Leaf. *Acc. Chem. Res.* **2012**, *45* (5), 767–776.
- (4) Armaroli, N.; Balzani, V. Solar Electricity and Solar Fuels: Status and Perspectives in the Context of the Energy Transition. *Chem. - Eur. J.* **2016**, *22* (1), 32–57.
- (5) Liu, C.; Colón, B. C.; Ziesack, M.; Silver, P. A.; Nocera, D. G. Water Splitting–Biosynthetic System with CO₂ Reduction Efficiencies Exceeding Photosynthesis. *Science* **2016**, *352*, 1210–1213.
- (6) Liu, C.; Sakimoto, K. K.; Colón, B. C.; Silver, P. A.; Nocera, D. G. Ambient Nitrogen Reduction Cycle Using a Hybrid Inorganic-Biological System. *Proc. Natl. Acad. Sci. U.S.A.* **2017**, *114*, 6450–6455.
- (7) Tamaki, Y.; Ishitani, O. Supramolecular Photocatalysts for the Reduction of CO₂. *ACS Catal.* **2017**, *7*, 3394–3409.
- (8) Woolerton, T. W.; Sheard, S.; Chaudhary, Y. S.; Armstrong, F. A. Enzymes and Bio-Inspired Electrocatalysts in Solar Fuel Devices. *Energy Environ. Sci.* **2012**, *5*, 7470.
- (9) Tyystjärvi, E. Photoinhibition of Photosystem II and Photo-damage of the Oxygen Evolving Manganese Cluster. *Coord. Chem. Rev.* **2008**, *252*, 361–376.
- (10) Aro, E.-M.; Virgin, I.; Andersson, B. Photoinhibition of Photosystem II. Inactivation, Protein Damage and Turnover. *Biochim. Biophys. Acta. Bioenerg* **1993**, *1143*, 113–134.
- (11) Thorarinsdottir, A. E.; Veroneau, S. S.; Nocera, D. G. Self-Healing Oxygen Evolution Catalysts. *Nat. Commun.* **2022**, *13* (1), 1243.
- (12) Crabtree, R. H. Deactivation in Homogeneous Transition Metal Catalysis: Causes, Avoidance, and Cure. *Chem. Rev.* **2015**, *115* (1), 127–150.
- (13) Najafpour, M. M.; Fekete, M.; Sedigh, D. J.; Aro, E. M.; Carpentier, R.; Eaton-Rye, J. J.; Nishihara, H.; Shen, J. R.; Allakhverdiev, S. I.; Spiccia, L. Damage Management in Water-Oxidizing Catalysts: From Photosystem II to Nanosized Metal Oxides. *ACS Catal.* **2015**, *5*, 1499–1512.
- (14) Du, P.; Schneider, J.; Li, F.; Zhao, W.; Patel, U.; Castellano, F. N.; Eisenberg, R. Bi- and Terpyridyl Platinum(II) Chloro Complexes: Molecular Catalysts for the Photogeneration of Hydrogen from Water or Simply Precursors for Colloidal Platinum? *J. Am. Chem. Soc.* **2008**, *130*, 5056–5058.
- (15) Ozawa, H.; Haga, M.; Sakai, K. A Photo-Hydrogen-Evolving Molecular Device Driving Visible-Light-Induced EDTA-Reduction of Water into Molecular Hydrogen. *J. Am. Chem. Soc.* **2006**, *128*, 4926–4927.
- (16) Whang, D. R.; Park, S. Y. Rational Design of an Electron-Reservoir Pt^{II} Complex for Efficient Photocatalytic Hydrogen Production from Water. *ChemSusChem* **2015**, *8*, 3204–3207.
- (17) Pfeffer, M. G.; Schäfer, B.; Smolentsev, G.; Uhlig, J.; Nazarenko, E.; Guthmüller, J.; Kuhnt, C.; Wächter, M.; Dietzek, B.; Sundström, V.; Rau, S. Palladium versus Platinum: The Metal in the Catalytic Center of a Molecular Photocatalyst Determines the Mechanism of the Hydrogen Production with Visible Light. *Angew. Chem. Int. Ed* **2015**, *54*, 5044–5048.
- (18) Kim, D.; Whang, D. R.; Park, S. Y. Self-Healing of Molecular Catalyst and Photosensitizer on Metal–Organic Framework: Robust Molecular System for Photocatalytic H₂ Evolution from Water. *J. Am. Chem. Soc.* **2016**, *138*, 8698–8701.
- (19) Yang, S.; Fan, D.; Hu, W.; Pattengale, B.; Liu, C.; Zhang, X.; Huang, J. Elucidating Charge Separation Dynamics in a Hybrid Metal–Organic Framework Photocatalyst for Light-Driven H₂ Evolution. *J. Phys. Chem. C* **2018**, *122*, 3305–3311.
- (20) Lazarides, T.; McCormick, T.; Du, P.; Luo, G.; Lindley, B.; Eisenberg, R. Making Hydrogen from Water Using a Homogeneous System without Noble Metals. *J. Am. Chem. Soc.* **2009**, *131* (26), 9192–9194.
- (21) McCormick, T. M.; Han, Z.; Weinberg, D. J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. Impact of Ligand Exchange in Hydrogen Production from Cobaloxime-Containing Photocatalytic Systems. *Inorg. Chem.* **2011**, *50*, 10660–10666.
- (22) Roy, S.; Bhunia, A.; Schuth, N.; Haumann, M.; Ott, S. Light-Driven Hydrogen Evolution Catalyzed by a Cobaloxime Catalyst Incorporated in a MIL-101(Cr) Metal–Organic Framework. *Sustain. Energy Fuels* **2018**, *2*, 1148–1152.
- (23) Huber-Gedert, M.; Nowakowski, M.; Kertmen, A.; Burkhardt, L.; Lindner, N.; Schoch, R.; Herbst-Irmer, R.; Neuba, A.; Schmitz, L.; Choi, T. K.; Kubicki, J.; Gawelda, W.; Bauer, M. Fundamental Characterization, Photophysics and Photocatalysis of a Base Metal Iron(II)-Cobalt(III) Dyad. *Chem. - Eur. J.* **2021**, *27*, 9905–9918.
- (24) Utschig, L. M.; Silver, S. C.; Mulfort, K. L.; Tiede, D. M. Nature-Driven Photochemistry for Catalytic Solar Hydrogen Production: A Photosystem I-Transition Metal Catalyst Hybrid. *J. Am. Chem. Soc.* **2011**, *133*, 16334–16337.
- (25) Kim, D.; Whang, D. R.; Park, S. Y. Self-Healing of Molecular Catalyst and Photosensitizer on Metal–Organic Framework: Robust Molecular System for Photocatalytic H₂ Evolution from Water. *J. Am. Chem. Soc.* **2016**, *138*, 8698–8701.
- (26) Li, J.; He, L.; Liu, Q.; Ren, Y.; Jiang, H. Visible Light-Driven Efficient Palladium Catalyst Turnover in Oxidative Transformations within Confined Frameworks. *Nat. Commun.* **2022**, *13*, 928.
- (27) Miloserdov, F. M.; McMullin, C. L.; Belmonte, M. M.; Benet-Buchholz, J.; Bakhmutov, V. I.; Macgregor, S. A.; Grushin, V. V. The Challenge of Palladium-Catalyzed Aromatic Azidocarbonylation: From Mechanistic and Catalyst Deactivation Studies to a Highly Efficient Process. *Organometallics* **2014**, *33*, 736–752.
- (28) Tabari, D. S.; Tolentino, D. R.; Schrodri, Y. Reactivation of a Ruthenium-Based Olefin Metathesis Catalyst. *Organometallics* **2013**, *32*, 5–8.
- (29) Lei, P.; Hedlund, M.; Lomoth, R.; Rensmo, H.; Johansson, O.; Hammarström, L. The Role of Colloid Formation in the Photo-induced H₂ Production with a Ru^{II}–Pd^{II} Supramolecular Complex: A Study by GC, XPS, and TEM. *J. Am. Chem. Soc.* **2008**, *130*, 26–27.
- (30) Hirose, T.; Maeno, Y.; Himeda, Y. Photocatalytic Carbon Dioxide Photoreduction by Co(bpy)₃²⁺ Sensitized by Ru(bpy)₃²⁺

Fixed to Cation Exchange Polymer. *J. Mol. Catal. A: Chemical* **2003**, *193*, 27–32.

(31) Romanenko, I.; Rajagopal, A.; Neumann, C.; Turchanin, A.; Streb, C.; Schacher, F. H. Embedding Molecular Photosensitizers and Catalysts in Nanoporous Block Copolymer Membranes for Visible-Light Driven Hydrogen Evolution. *J. Mater. Chem. A* **2020**, *8*, 6238–6244.

(32) Schneider, J.; Jia, H.; Muckerman, J. T.; Fujita, E. Thermodynamics and Kinetics of CO₂, CO, and H⁺ Binding to the Metal Centre of CO₂ reduction catalysts. *Chem. Soc. Rev.* **2012**, *41*, 2036–2051.

(33) Froehlich, J. D.; Kubiak, C. P. The Homogeneous Reduction of CO₂ by [Ni(Cyclam)]⁺: Increased Catalytic Rates with the Addition of a CO Scavenger. *J. Am. Chem. Soc.* **2015**, *137*, 3565–3573.

(34) Yu, B.; Li, L.; Liu, S.; Wang, H.; Liu, H.; Lin, C.; Liu, C.; Wu, H.; Zhou, W.; Li, X.; Wang, T.; Chen, B.; Jiang, J. Robust Biological Hydrogen-Bonded Organic Framework with Post-Functionalized Rhenium(I) Sites for Efficient Heterogeneous Visible-Light-Driven CO₂ Reduction. *Angew. Chem. Int. Ed* **2021**, *60*, 8983–8989.

(35) Jeong, D. C.; Lee, J.; Ro, Y. H.; Song, C. Repairable Photoactive Polymer Systems via Metal-Terpyridine-Based Self-Assembly. *Polym. Chem.* **2017**, *8*, 1923–1931.

(36) Kastner, K.; Lechner, M.; Weber, S.; Streb, C. In Situ Assembly, De-Metalation and Induced Repair of a Copper-Polyoxovanadate Oxidation Catalyst. *ChemistrySelect* **2017**, *2*, 5542–5544.

(37) Hill, C. L. Stable, Self-Assembling, Equilibrating Catalysts for Green Chemistry. *Angew. Chem. Int. Ed* **2004**, *43*, 402–404.

(38) Hill, C. L.; Zhang, X. A “smart” Catalyst That Self-Assembles under Turnover Conditions. *Nature* **1995**, *373*, 324–326.

(39) Weinstock, I. A.; Barbuzzi, E. M. G.; Wemple, M. W.; Cowan, J. J.; Reiner, R. S.; Sonnen, D. M.; Heintz, R. A.; Bond, J. S.; Hill, C. L. Equilibrating Metal-Oxide Cluster Ensembles for Oxidation Reactions Using Oxygen in Water. *Nature* **2001**, *414*, 191–195.

(40) Sloboda-Rozner, D.; Alsters, P. L.; Neumann, R. A Water-Soluble and “Self-Assembled” Polyoxometalate as a Recyclable Catalyst for Oxidation of Alcohols in Water with Hydrogen Peroxide. *J. Am. Chem. Soc.* **2003**, *125*, 5280–5281.

(41) Konduri, R.; Ye, H.; MacDonnell, F. M.; Serroni, S.; Campagna, S.; Rajeshwar, K. Ruthenium Photocatalysts Capable of Reversibly Storing up to Four Electrons in a Single Acceptor Ligand: A Step Closer to Artificial Photosynthesis. *Angew. Chem.* **2002**, *114*, 3317–3319.

(42) Staffilani, M.; Belsler, P.; De Cola, L.; Hartl, F. Redox Control of Conformation and Luminescence of a Dinuclear Ruthenium(II) Complex with a Bis-Dipyridophenazine Bridging Ligand. *Eur. J. Inorg. Chem.* **2002**, *2002*, 335–339.

(43) Konduri, R.; De Tacconi, N. R.; Rajeshwar, K.; MacDonnell, F. M. Multielectron Photoreduction of a Bridged Ruthenium Dimer, [(Phen)₂Ru(Tatpp)Ru(Phen)₂][PF₆]₄: Aqueous Reactivity and Chemical and Spectroelectrochemical Identification of the Photo-products. *J. Am. Chem. Soc.* **2004**, *126*, 11621–11629.

(44) McGovern, D. A.; Selmi, A.; O'Brien, J. E.; Kelly, J. M.; Long, C. Reduction of Dipyrido-[3,2-a:2',3'-c]-Phenazine (Dppz) by Photolysis in Ethanol Solution. *Chem. Commun.* **2005**, 1402–1404.

(45) Polyansky, D.; Cabelli, D.; Muckerman, J. T.; Fujita, E.; Koizumi, T.; Fukushima, T.; Wada, T.; Tanaka, K. Photochemical and Radiolytic Production of an Organic Hydride Donor with a Ru(II) Complex Containing an NAD⁺ Model Ligand. *Angew. Chem.* **2007**, *119*, 4247–4250.

(46) Polyansky, D. E.; Cabelli, D.; Muckerman, J. T.; Fukushima, T.; Tanaka, K.; Fujita, E. Mechanism of Hydride Donor Generation Using a Ru(II) Complex Containing an NAD⁺ Model Ligand: Pulse and Steady-State Radiolysis Studies. *Inorg. Chem.* **2008**, *47*, 3958–3968.

(47) Fukushima, T.; Fujita, E.; Muckerman, J. T.; Polyansky, D. E.; Wada, T.; Tanaka, K. Photochemical Stereospecific Hydrogenation of a Ru Complex with an NAD⁺/NADH-Type Ligand. *Inorg. Chem.* **2009**, *48*, 11510–11512.

(48) Kobayashi, K.; Ohtsu, H.; Nozaki, K.; Kitagawa, S.; Tanaka, K. Photochemical Properties and Reactivity of a Ru Compound Containing an NAD/NADH-Functionalized 1,10-Phenanthroline Ligand. *Inorg. Chem.* **2016**, *55*, 2076–2084.

(49) Lefebvre, J.-F.; Schindler, J.; Traber, P.; Zhang, Y.; Kupfer, S.; Gräfe, S.; Baussanne, I.; Demeunynck, M.; Mouesca, J.-M.; Gambarelli, S.; Artero, V.; Dietzek, B.; Chavarot-Kerlidou, M. An Artificial Photosynthetic System for Photoaccumulation of Two Electrons on a Fused Dipyridophenazine (Dppz)-Pyridoquinolinone Ligand. *Chem. Sci.* **2018**, *9*, 4152–4159.

(50) Sawaki, T.; Ishizuka, T.; Namura, N.; Hong, D.; Miyanishi, M.; Shiota, Y.; Kotani, H.; Yoshizawa, K.; Jung, J.; Fukuzumi, S.; Kojima, T. Photocatalytic Hydrogen Evolution Using a Ru(II)-Bound Heteroaromatic Ligand as a Reactive Site. *Dalton Trans* **2020**, *49*, 17230–17242.

(51) Pfeffer, M. G.; Müller, C.; Kastl, E. T. E.; Mengele, A. K.; Bagemihl, B.; Fauth, S. S.; Habermehl, J.; Petermann, L.; Wächtler, M.; Schulz, M.; Chartrand, D.; Laverdière, F.; Seeber, P.; Kupfer, S.; Gräfe, S.; Hanan, G. S.; Vos, J. G.; Dietzek-Ivanšić, B.; Rau, S. Active Repair of a Dinuclear Photocatalyst for Visible-Light-Driven Hydrogen Production. *Nat. Chem.* **2022**, *14*, 500–506.

(52) Pla, P.; Wang, Y.; Martín, F.; Alcamí, M. Hydrogenated Polycyclic Aromatic Hydrocarbons: Isomerism and Aromaticity. *Phys. Chem. Chem. Phys.* **2020**, *22*, 21968–21976.

(53) Schweitzer, C.; Schmidt, R. Physical Mechanisms of Generation and Deactivation of Singlet Oxygen. *Chem. Rev.* **2003**, *103*, 1685–1757.

(54) McDaniel, N. D.; Bernhard, S. Solar Fuels: Thermodynamics, Candidates, Tactics, and Figures of Merit. *Dalton Trans* **2010**, *39*, 10021–10030.

(55) Kinik, F. P.; Nguyen, T. N.; Oveisi, E.; Valizadeh, B.; Ebrahim, F. M.; Gladysiak, A.; Mensi, M.; Stylianou, K. C. Discovery of a Self-Healing Catalyst for the Hydrolytic Dehydrogenation of Ammonia Borane. *J. Mater. Chem. A* **2019**, *7*, 23830–23837.

(56) Zhang, G.; Wu, Z.; Liu, H.; Ji, Q.; Qu, J.; Li, J. Photoactuation Healing of α -FeOOH@g-C₃N₄ Catalyst for Efficient and Stable Activation of Persulfate. *Small* **2017**, *13*, 1702225.

(57) Barros Barbosa, J.; Taberna, P. L.; Bourdon, V.; Gerber, I. C.; Poteau, R.; Balocchi, A.; Marie, X.; Esvan, J.; Puech, P.; Barnabé, A.; Da Gama Fernandes Vieira, L.; Moraru, I. T.; Chane-Ching, J. Y. Mo Thio and Oxo-Thio Molecular Complexes Film as Self-Healing Catalyst for Photocatalytic Hydrogen Evolution on 2D Materials. *Appl. Catal., B* **2020**, *278*, 119288.

(58) Wen, C.; Dunbar, D.; Zhang, X.; Lauterbach, J.; Hatrick-Simpers, J. Self-Healing Catalysts: Co₃O₄ Nanorods for Fischer-Tropsch Synthesis. *Chem. Commun.* **2014**, *50*, 4575–4578.

(59) Kanan, M. W.; Surendranath, Y.; Nocera, D. G. Cobalt-Phosphate Oxygen-Evolving Compound. *Chem. Soc. Rev.* **2009**, *38*, 109–114.

(60) Ullman, A. M.; Brodsky, C. N.; Li, N.; Zheng, S.-L.; Nocera, D. G. Probing Edge Site Reactivity of Oxidic Cobalt Water Oxidation Catalysts. *J. Am. Chem. Soc.* **2016**, *138*, 4229–4236.

(61) Costentin, C.; Nocera, D. G. Self-Healing Catalysis in Water. *Proc. Natl. Acad. Sci. U.S.A* **2017**, *114*, 13380–13384.

(62) Surendranath, Y.; Lutterman, D. A.; Liu, Y.; Nocera, D. G. Nucleation, Growth, and Repair of a Cobalt-Based Oxygen Evolving Catalyst. *J. Am. Chem. Soc.* **2012**, *134*, 6326–6336.

(63) Kanan, M. W.; Nocera, D. G. In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co²⁺. *Science* **2008**, *321*, 1072–1075.

(64) Surendranath, Y.; Dincă, M.; Nocera, D. G. Electrolyte-Dependent Electrosynthesis and Activity of Cobalt-Based Water Oxidation Catalysts. *J. Am. Chem. Soc.* **2009**, *131*, 2615–2620.

(65) Du, P.; Kokhan, O.; Chapman, K. W.; Chupas, P. J.; Tiede, D. M. Elucidating the Domain Structure of the Cobalt Oxide Water Splitting Catalyst by X-Ray Pair Distribution Function Analysis. *J. Am. Chem. Soc.* **2012**, *134*, 11096–11099.

(66) Huynh, M.; Bediako, D. K.; Nocera, D. G. A Functionally Stable Manganese Oxide Oxygen Evolution Catalyst in Acid. *J. Am. Chem. Soc.* **2014**, *136*, 6002–6010.

(67) Bediako, D. K.; Surendranath, Y.; Nocera, D. G. Mechanistic Studies of the Oxygen Evolution Reaction Mediated by a Nickel–Borate Thin Film Electrocatalyst. *J. Am. Chem. Soc.* **2013**, *135*, 3662–3674.

(68) Huynh, M.; Ozel, T.; Liu, C.; Lau, E. C.; Nocera, D. G. Design of Template-Stabilized Active and Earth-Abundant Oxygen Evolution Catalysts in Acid. *Chem. Sci.* **2017**, *8*, 4779–4794.

(69) Wang, J.; Ji, L.; Chen, Z. In Situ Rapid Formation of a Nickel–Iron-Based Electrocatalyst for Water Oxidation. *ACS Catal.* **2016**, *6*, 6987–6992.

(70) Feng, C.; Wang, F.; Liu, Z.; Nakabayashi, M.; Xiao, Y.; Zeng, Q.; Fu, J.; Wu, Q.; Cui, C.; Han, Y.; Shibata, N.; Domen, K.; Sharp, I. D.; Li, Y. A Self-Healing Catalyst for Electrocatalytic and Photoelectrochemical Oxygen Evolution in Highly Alkaline Conditions. *Nat. Commun.* **2021**, *12*, 5980.

(71) Kuang, Y.; Jia, Q.; Ma, G.; Hisatomi, T.; Minegishi, T.; Nishiyama, H.; Nakabayashi, M.; Shibata, N.; Yamada, T.; Kudo, A.; Domen, K. Ultrastable Low-Bias Water Splitting Photoanodes via Photocorrosion Inhibition and in Situ Catalyst Regeneration. *Nat. Energy* **2017**, *2*, 16191.