Photo- and electrocatalytic H₂ evolution with cobalt oxime complexes

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Converting sunlight into storable chemical energy carriers, such as dihydrogen (H₂), through light-driven splitting of water is a widely studied approach to secure future energy supplies and sustainability. Molecular complexes based on inexpensive and earth-abundant 3d transition metals have been extensively explored as catalysts for the reduction of water to H₂. Among these, cobalt complexes with an oxime functionality (*i.e.*, cobaloxime and cobalt diimine-dioxime) efficiently reduce protons in pure water with low to moderate overpotentials, and they have been shown to remain active under aerobic conditions. Based on their simple and straightforward synthesis in addition to their excellent electrochemical properties, they are often applied as the first-choice catalyst when testing new materials or introducing new concepts for H₂ evolution. In this review, their basic electrochemical and electrocatalytic properties as well as mechanistic investigations will be summarized, followed by an overview of their application in photocatalysis. Finally, their integration with (nano)materials for (photo)electrocatalytic H₂ evolution is presented and discussed.

1. Introduction

1.1. Challenges and Motivation

Our economy currently faces an energy crisis due to a predicted shortage of fossil resources, significant rise in carbon dioxide levels, and an unequal distribution of energy resources provoking political conflicts.¹ Using abundant sunlight to generate solar fuels and chemical feedstocks sustainably from water or CO₂ is a promising strategy to tackle these challenges, and secure independent future energy supplies.^{2–4} For example, light-driven splitting of water generates dihydrogen (H₂), an energy-dense molecule and important feedstock for the chemical industry.^{5,6}

Approaches to achieve solar H₂ generation from water include photovoltaic (PV) modules coupled to a water electrolyzer,^{7,8} photoelectrochemical (PEC) devices,^{9–12} or other artificial photosynthetic systems.^{13,14} In all three systems, electrons and holes generated by a light absorber must be transferred to defined catalytic sites, where the proton reduction and water oxidation processes occur. Usually, a

combination of different compounds or materials is used to accomplish water splitting in those devices or systems ranging from synthetic molecular complexes, isolated bio-molecules, such as enzymes or proteins, and living cells, to organic and inorganic (nano)materials.^{10,12,15–18}

Molecular complexes are often designed as enzyme active site mimics,^{19,20} or their design is at the least enzyme-inspired by integrating the enzyme's essential structural or functional features.^{21,22} As in enzymes, molecular catalysis takes place at a well-defined active site usually with a high selectivity for a certain reaction, *e.g.* CO₂ reduction,²³ in contrast to (nano)materials where the true active site is often unknown, and therefore improving selectivity is challenging.²⁴ In molecular complexes, these active sites can be easily further modified, which allows one to tune their catalytic activity, investigate the catalytic mechanism, or study structure-activity relationships.^{25,26}

For the H₂ evolution reaction, a vast number of molecular complexes has been reported in past decades, with many being based on 3d transition metals, such as Fe,^{27–29} Co,^{30–35} or Ni.^{36–41} They have been applied in a variety of different electro- and photocatalytic schemes, and efforts have also been made to integrate them with materials to prepare devices for (light-driven) H₂ evolution.^{42–47} Herein, the application of cobalt oxime complexes as catalysts in such systems is reviewed.

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1.2. Cobalt oxime complexes

Cobalt complexes containing a tetradentate dimethylglyoximate-dimethylglyoxime (dmgH)(dmgH₂), bis(dimethylglyoximate) (dmgH)₂, or *N,N'*-propanediyl-bis(2,3-butanedione-2-imine-3-oxime) ligand, ((DO)(DOH)pn) (Fig. 1), as equatorial ligand, have long been identified as active molecular catalysts for the reduction of aqueous protons.^{48–53} Initially designed as vitamin B12 models,^{54–56} a few studies on their proton reduction properties were reported in the 1970s and 1980s.^{48,49} They were re-investigated for catalytic H₂ evolution approximately two decades later,^{50,51,57} and, to date, there is a wealth of experimental and theoretical information available for these types of H₂ evolution catalysts.^{25,50,58–65} These so-called cobaloximes ((dmgH)₂-type) and cobalt diimine-dioximes ((DO)(DOH)pn-type) operate with low to moderate overpotentials in organic solvents^{51,65} and even in pure water.^{52,66} They are also among the very few synthetic catalysts that have been reported as being O₂-tolerant during H₂ evolution catalysis – an important consideration for their application in full water-splitting systems where oxygen is generated at the anodic side of a device.^{66–68}

Fig. 1 General chemical structures of cobaloxime (A and B) and cobalt diimine-dioxime complexes (C). X = ligand (e.g. halide, solvent).

1.2.1 Electrochemical properties

Thorough electrochemical investigations have shown that cobaloximes ((dmgH)₂-type; Fig. 1A and B) function well as H₂ evolution catalysts in a pH range of 6 to 8 in water, with onset potentials (η) as low as -0.1 V vs. RHE (reversible hydrogen electrode). In bulk experiments, they produce H₂ at overpotentials of a few hundred mV (approx. 200 to 300 mV) with good faradaic efficiencies (FE > 60%).^{25,66} The overpotential can be reduced by introducing an axial pyridine ligand, and the catalytic rates can be easily tuned by the choice of R on the pyridine ligand; e.g., pyridine ligands with an electron-donating substituent R were found to increase the rate of catalysis.^{25,51} The additional benefit that they can be readily prepared from cobalt salts, dimethylglyoxime and an optional axial pyridine ligand,^{25,64} makes cobaloximes readily-accessible first targets to screen new materials for (photo) catalytic proton reduction.

In cobalt diimine-dioximes ((DO)(DOH)pn-type; Fig. 1C), one of the oxime bridges is replaced by a propanediyl bridge, which provides the complex with better stability, and allows them to be employed as proton reduction catalysts at lower pH values where cobaloximes are normally unstable.⁶⁵ The cobalt diimine-dioxime catalysts feature slightly more negative onset potentials for proton reduction in water (η > 250 mV) than cobaloximes.^{52,69} However, they can adapt to the specific conditions used, keeping the required overpotential within a small margin over a wider pH range.^{26,65} More acidic conditions were generally found to be beneficial for overall catalyst activity.^{16,52} In prolonged electrolysis solution experiments, cobalt diimine-dioximes showed good FE (>80%).^{52,69}

While a more negative applied potential during electrolysis (*i.e.* more available driving force) would normally lead to an increase in TOF_{cat},⁷⁰ the potential window where cobalt oximes operate as true molecular catalysts is limited for both types of complexes. At potentials that are too negative, the reduced molecular complexes readily decompose into different metal-containing species, sometimes found to be the active species for H₂ evolution.^{71,72}

1.2.2 H₂ evolution mechanism

The proton reduction mechanism of cobalt oxime complexes has been the scope of numerous experimental and computational studies, and proceeds *via* several successive, potentially coupled reduction and protonation steps (Fig. 2), which involve metal (gray) as well as possible ligand protonation (bold).^{59,73} Although the overall catalytic mechanism to release H₂ has been controversially discussed, there is consensus that the initial Co^{III} complex, [Co^{III}L]⁺, is first reduced to [Co^{II}L] (Fig. 2A).⁷⁴ Upon this initial reduction of the inert low-spin Co^{III} complex to a labile Co^{II} species, one of the axial ligands of the octahedral complex is released, giving a penta-coordinated complex with a vacant coordination site for catalysis.⁵¹ Depending on the conditions (e.g., aqueous pH or pK_a of the proton source in organic solvents), the Co^{II} species is then either directly reduced to [Co^IL] (Fig. 2A, top), or forms a ligand-protonated [Co^ILH] species (Fig. 2A, bottom).^{59,63} In both cases, this is followed by protonation of the metal center to give a Co^{III}-hydride species, [Co^{III}HL] or [Co^{III}HLH]⁺.⁶⁰ While cobalt oximes would follow the classical route without protonation of the oxime ligand under near neutral conditions, the ligand-protonated pathway may play a role at lower pH values (cobalt diimine-dioximes only).⁵⁹ Protonation of the diimine-dioxime ligand aids reduction of the intermediate species due to the additional positive charge, and would account for the pH-dependent anodic shift of

the proton reduction overpotential that has been repeatedly observed for cobalt diimine-dioxime complexes.^{26,52,63,65}

Some studies have suggested that the final H₂-evolving steps require a proton and one Co^{III}-hydride species (heterolytic, monometallic, Fig. 2B),^{51,61,75,76} whereas others have proposed a homolytic bimolecular pathway with two Co^{III}-hydride species being involved in H₂ formation (Fig. 2C).^{50,77–79} However, the heterolytic pathway is the generally preferred route, and the protonation of the Co-hydride was identified as the rate-limiting step of catalysis in this case.^{58,74,78} Nevertheless, homolytic generation of H₂ might be favored under very specific conditions, such as a high concentration of the catalyst and low proton concentration (near neutral pH). Computational studies have shown that the Co^{III}H/Co^{II}H reduction happens at a more positive potential than the Co^{II}/Co^I reduction,⁶⁰ which suggests that further reduction of the intermediate Co^{III}-hydride species occurs, and H₂ evolution most likely proceeds *via* a Co^{II}-hydride (bottom pathway in Fig. 2B and C).^{74,80,81}

Direct experimental and theoretical evidence for an intermediate Co^{III}-hydride species in the form of a [Co^{III}H(dmgH)₂P(*n*-Bu)₃] complex^{54,82} has been under debate as this original assignment was likely based on a paramagnetic impurity.⁸³ Furthermore, claims of positioning of the active hydrogen on the oxime ligand with the possibility for tautomerization to the metal-centred hydride⁸⁴ highlight that further investigations to solidify current mechanistic interpretations are required.

1.2.3 O₂-tolerant proton reduction

Fig. 2 Proposed H₂ evolution mechanisms for cobaloxime and cobalt diimine-dioxime complexes. (A) Consecutive reduction and protonation steps; gray: classical pathway with protonation of the metal centre only; bold: bridge-protonated pathway which involves protonation of the oxime O-H-O functionality. Final H₂ evolution step, only shown for classical pathway; (B) heterolytic monometallic pathway where protonation occurs at one cobalt-hydride species; (C) homolytic bimolecular pathway which requires two hydride species; L = ((DO)(DOH)pn) or (dmgH)₂; possible axial ligands such as halides or solvent molecules are omitted for clarity.

Several electrochemical and photocatalytic studies have shown that both types of catalyst are able to reduce protons efficiently even in the presence of O₂.^{66,68,85,86} In prolonged electrolysis experiments, they kept between 25–50% of their activity under atmospheric O₂ levels, or in O₂-saturated solution, in comparison to an inert N₂ atmosphere; however, with somewhat lower faradaic efficiencies for H₂. This loss in efficiency can be attributed to the competing reduction of O₂ by the catalyst itself when in its Co^{II} state (Fig. 3A). When reaching the Co^I state, the higher concentrations of protons in comparison to O₂ are in favor for the H₂ evolution reaction to take place instead of the competing oxygen reduction reaction. Notably, the catalyst remains operational even in the presence of intermediate reactive oxygen species (ROS), which have been shown to decompose other molecular catalysts (Fig. 3B).⁶⁸ Cobalt oximes can therefore also be described as oxygen-tolerant catalysts, similar to some oxygen-tolerant hydrogenases found in nature.⁸⁷

Fig. 3 (A) Schematic representation of the heterolytic H₂ evolution and potential O₂ reduction pathways; (B) Schematic representation of the two potential routes upon exposure of a catalyst to O₂. Adapted from ref 87.

2. Photocatalytic H₂ evolution

A plethora of different systems for photocatalytic H₂ evolution based on cobalt oxime complexes have been reported in the past decade.^{32,88} The systems can be divided into homogeneous systems, with both the catalyst and a molecular dye in solution, semi-heterogeneous systems,⁴² where a semiconductor is used as a light-absorber, or dye-sensitized photocatalysis (DSP) systems where a molecular catalyst and dye are linked to a semiconducting particle. The components of the first two photocatalytic systems could both be freely diffusing in solution (Fig. 4, diffusional), or be linked to one another by covalent or non-covalent interactions (Fig. 4, linked). The DSP approach co-immobilizes a molecular catalyst and dye on a semiconducting (nano)particle (Fig. 4, DSP).⁸⁹ In this case, the semiconductor functions as a scaffold to bring the molecular components in close

proximity, and to improve electron transfer dynamics from the dye to the catalyst through effective charge separation. In all systems, matching of the excited state potential or conduction band (CB) potential of semiconductor to the proton reduction onset potential of the catalyst is an important thermodynamic consideration.

Fig. 4 Schematic representation of photocatalytic systems for H_2 evolution. Electron transfer can occur between the components diffusing in solution or when linked to each other. The dye-sensitized photocatalysis (DSP) approach (bottom) employs a molecular dye on a semiconductor (SC) particle with a co-adsorbed catalyst (cat). SED = sacrificial electron donor.⁸⁹

2.1. Homogeneous systems

2.1.1 Diffusional systems

The first photocatalytic system using the cobaloxime complex **1** (Fig. 5) was reported in 1983, where it was combined with the $[\text{Ru}(\text{bpy})_3]^{2+}$ light-absorber **6** (bpy = 2,2'-bipyridine; Fig. 6) in a water/organic solvent mixture in the presence of a sacrificial reagent.⁴⁸ Subsequently, H_2 evolution by the cobaloxime complexes **1**, **2** and **3** ($\text{R} = \text{H}$) was observed either with the Pt-based chromophore **7**,^{57,90} or Re-based photosensitizers **8** and **9** ($\text{Y} = \text{Br}$)^{75,91,92} in water/acetonitrile mixtures or pure organic solvents in the presence of a proton source, respectively. Cobalt-based turnover numbers (TON_{Co}) of up to 273 were achieved using **2** and **8** in an acetone solution with triethylamine (TEA) as SED and TEA-H^+ as proton source.⁷⁵

Replacing the Pt- and Re-based dyes by either organic eosin-Y/rose bengal derivatives (**10**, Fig. 6),⁷⁹ or the water-soluble Zn-porphyrin sensitizer **11**⁹³ created noble-metal-free systems. The cobaloxime complex with an axial pyridine ligand (**3**, $\text{R} = \text{H}$) was used as a catalyst in both studies. Photocatalytic H_2 evolution was observed from water/

acetonitrile mixtures (1:1) with triethanolamine (TEOA, 5% v/v) as the sacrificial reagent, achieving TON_{Co} between 23 (with **11**) and 180 (with **10** and excess ligand). The Zn-porphyrin dye was also used to elucidate the effect of various axial *N*-donor ligands, in particular the effect of different para-substituted pyridine ligands, on the initial activity and long-term stability of the homogeneous photocatalytic system.⁶⁴ Electron-rich axial ligands were generally found to have a positive influence on the overall performance. This partially agrees with electrochemical studies, where axial electron-donating pyridine ligands resulted in faster rates for catalysis.^{25,51} TON_{Co} of up to approximately 80 were reported for the pyridine-substituted cobaloxime complex **3** ($\text{R} = \text{H}$) in combination with boron-dipyrromethene (BODIPY) chromophores (**12**, Fig. 6) and TEOA as donor (5% v/v), but again from a water/acetonitrile mixture (2:3).⁹⁴ More recently, H_2 evolution from pure water (pH 7 TEOA solution) has been reported with para-substituted pyridines as axial ligand of the cobaloxime (**3**, $\text{R} = \text{PO}(\text{OH})_2$ and OMe) and eosin-Y as light-absorber (**10**, $\text{R}^1, \text{R}^2 = \text{Br}$, $\text{X} = \text{H}$), achieving up to approximately 75 TON_{Co} .^{25,66} Remarkably, this system also kept about 70% of its activity under an O_2 atmosphere.

Photocatalytic H_2 evolution with different cobalt diimine-dioxime complexes (**4** and **5**, Fig. 5) and rhenium photosensitizers (**8** and **9**, Fig. 6) was investigated using TEOA as SED at neutral and slightly basic pH values. A maximum TON_{Co} of 17 was reported for light-driven H_2 evolution ($\lambda = 380 \text{ nm}$) under purely aqueous conditions for the pyridine-functionalized complex **5**.⁹⁵ The activity of the complex $[\text{CoBr}_2(\text{DO})(\text{DOH})\text{pn}]$ (**4**, $\text{R}^1 = \text{R}^2 = \text{H}$) was improved under more acidic conditions using ascorbic acid (AA, pH 4.5) as SED and **8** as photosensitizer, achieving a maximum TON_{Co} of 90.⁵³ A similar TON_{Co} of 56 ± 12 was obtained with **4** using amorphous carbon nanodots (CDs) as

Fig. 5 Chemical structures of molecular cobaloxime (**1-3**) and cobalt diimine-dioxime complexes (**4** and **5**).

Fig. 6 Chemical structures of molecular dyes used as photosensitizer in combination with the molecular cobalt catalysts shown in Fig. 5: $[\text{Ru}(\text{bpy})_3]^{2+}$ (**6**), Pt-based chromophore (**7**), $[\text{Re}(\text{phen})(\text{CO})_3\text{Y}]^{+0}$ (**8**, phen = phenanthroline) and $[\text{Re}(\text{bpy})(\text{CO})_3\text{Y}]^{+0}$ (**9**), eosin-Y/rose bengal derivatives (**10**), Zn-porphyrin (**11**), BODIPY chromophores (**12**), and a cyclometalated Ir-based sensitizer (**13**).

light absorber in a so-called donor recycling system consisting of AA (pH 5) and tris-(2-carboxyethyl) phosphine (TCEP) as SED after 24 h of full spectrum solar irradiation (100 mW cm⁻²).⁹⁶ An enhanced long-term performance of the complex was reported upon the addition of PPh₃.⁹⁷ Final TON_{Co} of up to 700 were obtained with the Ir-based photosensitizer **13** (Fig. 6) and TEA (10%) as SED, but a water/acetonitrile mixture (1:1) was employed.

2.1.2 Linked systems

Tethering the catalyst core to the light-absorbing unit avoids limitations from diffusion-controlled kinetics, and should thereby improve the electron transfer (ET) kinetics from the dye to the catalyst after photo-excitation, resulting in increased performance. In most supramolecular systems based on cobaloxime complexes, the photosensitizer unit was connected to the catalyst *via* the axial pyridine ligand. Assemblies with Ru-based and cyclometalated iridium photosensitizers have been reported (**14–19**, Fig. 7).^{62,75,98} In the case of precious-metal-free supramolecular systems (Fig. 8), cobaloximes have been linked to porphyrins (**20**),^{99–101} fluorescein (**21**),¹⁰² BODIPY chromophores (**22**),^{103–106} and organic donor-acceptor dyes (**23**).¹⁰⁷

While fast intramolecular ET from the photoexcited light-absorber to the catalyst was observed, charge recombination also occurred on fast (ps to ns) timescales.^{99,107,108} Most of the systems showed only limited or a complete lack of H₂ evolution activity, offering no improvement in comparison to the corresponding multi-component systems, and several required the use of organic solvents for photoactivity. In addition, synthesis of the dyad molecules is synthetically challenging, and they often feature limited solubility, especially in water. Dissociation of the supramolecular assembly was also frequently observed after reduction of the catalyst due to a labile pyridine-Co bond, leading to a loss of the catalytic core from the light-absorbing unit.¹⁰⁷

Fig. 7 Examples of supramolecular assemblies for homogeneous photocatalysis with the cobaloxime catalyst covalently linked to Ru-based (**14–16**, **18**, **19**) or cyclometalated iridium photosensitizer (**17**).

Fig. 8 Examples of supramolecular assemblies for homogeneous photocatalysis with the cobaloxime catalyst linked to a precious-metal-free photosensitizer: porphyrins (**20**), fluorescein (**21**), BODIPY (**22**), and an organic donor-acceptor dye (**23**, perylene-1,8-naphthalimide, sol = solvent).

2.2. Semi-heterogeneous systems

Commonly used light-absorbers in semi-heterogeneous systems with molecular catalysts are cadmium chalcogenide quantum dots (CdX QDs, X = S, Se or Te),^{109–111} but other light-absorbing materials such as organic polymers (carbon nitrides),^{42,112} and (dye-sensitized) metal and covalent organic frameworks (MOFs and COFs, respectively) have been explored as well.^{113–115}

Light-driven H₂ evolution with cobaloximes (**3**, R = H, PO(OH)₂ and NMe₂, Fig. 5; **24**, Fig. 9) and Cd-containing QDs was achieved in organic solvent/water mixtures with TEOA or methanol as electron donor (TON_{Co} up to 171 in DMF/10 vol% water).^{116–118} It was shown that the initial H₂ production rate can be increased when using the thiolated derivative **24**, which was attributed to better association of the complex with the surface of the CdS QDs used therein (linked system).¹¹⁶ However, anchoring of the complex by the ortho-substituted pyridine might not be ideal, and could possibly be further improved. In a different study, fast ET on the ps timescale from photoexcited CdSe/ZnS core shell particles to a cobaloxime catalyst, linked to the particle surface *via* a phosphonic acid group, was observed by TAS.¹¹⁷ H₂ was produced from a toluene/TEOA solution with this CdSe/ZnS/cobaloxime hybrid. In some cases, an induction period and/or an increase in H₂ evolution over time were observed.^{117,118} These observations raise questions about the stability of the molecular catalyst and the nature of the catalytically active species,¹¹⁹ especially under harsh experimental conditions (e.g. pH 13.5), or when a large overpotential is applied to the catalyst (e.g. CB(CdSe) = −0.95 V vs. NHE). For the latter conditions, it has been shown that cobaloxime complexes are highly susceptible to degradation into other active cobalt-containing species.^{71,72,119}

Graphitic carbon nitride was tested with a pyridine-containing cobaloxime catalyst (**3**, R = H, Fig. 5), and H₂

was produced from aqueous solution under full spectrum irradiation ($\text{TON}_{\text{Co}} < 10$).¹²⁰ A higher TON_{Co} was obtained for the same catalyst in acetonitrile/water mixtures, and this system could be further improved when using a pyrene-functionalized cobaloxime (**25**, Fig. 9) to form a linked system.¹²¹ The π - π interaction between the pyrene moiety and the carbon nitride was claimed to promote ET from the reductively quenched light-absorber to the catalyst, thereby improving the photocatalytic performance.

In the case of cobalt diimine-dioximes, a semiheterogeneous composite consisting of the complex $[\text{CoBr}_2(\text{DO})(\text{DOH})\text{pn}]$ (**4**, $\text{R}^1 = \text{R}^2 = \text{H}$, Fig. 5) and a Ti-containing MOF as light-absorber has been reported for light-driven H_2 evolution.¹¹⁴ The MOF was prepared hydrothermally from titanium isopropoxide and 2-aminoterephthalic acid. The complex was incorporated by immersing the Ti-MOF in a solution of the diimine-dioxime ligand, followed by addition of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ to form the final complex. This composite was reported to evolve H_2 photocatalytically from acetonitrile with TEOA as donor achieving a $\text{TON}_{\text{Co}} \approx 10$ after 24 h.¹¹⁴

Fig. 9 Cobaloxime complexes used in molecular dye-free semiheterogeneous photocatalysis.^{116,121}

A variety of different photocatalytic systems with cobaloximes and cobalt diimine-dioximes as H_2 evolution catalysts have been reported. Most systems still required the use or at least addition of organic solvents, which is often due to a limited solubility of the components in water. In addition, limitations occurred from slow ET or fast charge recombination between the light absorber and the cobalt oxime catalyst, especially in the case of linked homogeneous systems.

2.3. Dye-sensitized semiconductor systems

Complexes **26–28** have been applied as catalysts in dye-sensitized photocatalysis (DSP) schemes (Fig. 4 and 10).^{26,122–124} The catalysts were co-immobilized on P25 TiO_2 nanoparticles with the Ru-dye **29** via its phosphonic acid functionalities.^{122,123} The cobaloxime catalyst **26** produced H_2 with a TON_{Co} up to approximately 110 on dye-sensitized

TiO_2 under visible light irradiation ($\lambda > 420$ nm, AM 1.5G 100 mW cm^{-2}) in purely aqueous pH 7 TEOA solution.¹²³ The degradation of the molecular cobaloxime catalyst was identified to limit the long-term performance of the system. By adding excess dmgH_2 ligand, it was possible to increase the long-term performance, and achieve $\text{TON}_{\text{Co}} > 300$.¹²⁵ No H_2 was produced in the absence of TiO_2 , strongly emphasizing the beneficial effect of the semiconductor on charge separation and productive electron transfer from the dye to the catalyst.^{125,126} Transient absorption spectroscopy revealed that a long-lived (up to 1 s), low potential TiO_2 conduction band (CB) electron is generated in this arrangement, which initiates H_2 evolution catalysis *via* reduction of the molecular complex.^{125,126} In addition, binding of the catalyst and dye to the TiO_2 surface was essential for good DSP performance during visible light exposure.¹²³

When replacing the Ru-based light-absorber with an organic diketopyrrolopyrrole dye (**30**, Fig. 10), a TON_{Co} of 17 was achieved for catalyst **26** in this precious-metal-free TiO_2 assembly.¹²⁴ The lower TON_{Co} was mainly attributed to poor regeneration of the oxidized organic dye by the SED TEOA after electron injection into the TiO_2 particle.

With the diphosphonated diimine-dioxime complex **27**, no H_2 was obtained in the dye-sensitized TiO_2 assembly, most likely due to a mismatch of the TiO_2 -CB and the catalytic onset potential for proton reduction of the catalyst.^{26,69} Introduction of a pyridine ligand (**28**, Fig. 10) allowed for lowering of the required overpotential for proton reduction by approximately 70 mV, and a TON_{Co} of 22 and 40 was obtained in pH 7 TEOA and pH 4.5 AA solution under visible light irradiation ($\lambda > 420$ nm, AM 1.5G 100 mW cm^{-2}), respectively.²⁶ Depending on the specific conditions used, the pyridine can influence the catalyst in two distinct ways: it can either enhance catalysis *via* coordination to the Co^{III} -hydride species, generating a more basic hydride, or act as a proton relay providing protons in proximity to the catalytically active

Fig. 10 Phosphonated cobaloxime (**26**) and cobalt diimine-dioxime (**27** and **28**) catalysts as well as dyes (**29** and **30**) used in dye-sensitized photocatalysis.^{26,69,122,124}

site.^{25,127}

■ ■ 3. (Photo)electrocatalytic H₂ evolution

To date, the vast majority of photocatalytic H₂ evolution systems with molecular catalysts relies on the use of sacrificial reagents. Ultimately, SEDs must be replaced to allow for sustainable solar fuels synthesis, and the development of full water splitting systems is of high priority. To achieve this goal, molecular H₂ evolution catalysts have been immobilized on (semi)conducting electrode materials (Fig. 11A) or photocathodes (Fig. 11B), and several operational hybrid devices for (photo) electrochemical H₂ evolution have been reported.^{128–130} In the case of photocathodes, the catalyst's onset potential for proton reduction has to be matched with the thermodynamic potentials of the light-absorbing part of the electrode, which could be a molecular dye, a light-absorbing material (e.g. quantum dots) or light-absorbing semiconductor (Fig. 11B, left and right, respectively). Such devices could then be wired, for example, to a water oxidation photoanode to achieve full light-driven water splitting without the need for a SED.^{10,12,131}

Fig. 11 Schematic representation of hybrid electrodes with molecular catalysts: (A) Hybrid cathode with a molecular catalyst immobilized on a (semi)conducting scaffold; (B) left: sensitized photocathode where the molecular catalyst and light-absorber are integrated with a semiconducting layer; right: photocathode with a molecular catalyst anchored to a light-absorbing semiconductor (SC); TCO = transparent conducting oxide; VB = valence band; CB = conduction band.

Hybridization attempts with solid-state materials, such as dye-sensitized TiO₂ in DSP,⁸⁹ confirmed that cobalt oximes can remain active once anchored to a surface, and integration with a variety of other (semi)conducting materials for electrocatalytic proton reduction has since been reported. These studies allow for a fundamental understanding of the behavior and activity of heterogenized catalysts to be obtained before moving towards molecular catalyst-modified photocathodes and full water splitting devices.

3.1. Cobalt oximes on electrodes

A monomeric and a polymer-embedded cobaloxime with a pyrene functionality (**31** and **32**, respectively, Fig. 12) were integrated with free-standing multi-walled carbon nanotube

(MW-CNT) electrodes. The MW-CNTs were chosen because of their good conductivity, and the possibility to provide a large surface area allowing for high catalyst loadings. These so-called bucky-papers were tested for electrocatalytic H₂ evolution in pH 6.5 phosphate buffer under inert and aerobic conditions.⁸⁵ The polymer scaffold led to an increased stability of the hybrid electrode, giving a TON_{Co} of 420 after 25 h of controlled potential electrolysis (CPE) at −0.7 V vs. NHE (normal hydrogen electrode; −0.32 V vs. RHE) compared to a TON_{Co} of 80 for the monomer. The better performance can be explained by stabilization from polymer-embedding, partially trapping the cobaloxime core after release from the pyridine group due to the labile Co–N bond during catalysis (Co^{II} and Co^I state). Notably, approximately 40 to 50% of the activity remained under atmospheric O₂ levels, and XPS discounted for the formation of active cobalt-based deposits during electrolysis.⁸⁵

A similar immobilization approach was applied for a cobaloxime complex featuring a diacetylene unit on the axial pyridine ligand (**33**, Fig. 12).¹³² The hydrophobic tail can interact with MW-CNTs, and the individual cobaloxime units on the CNTs were cross-linked by light-induced polymerization of the diacetylene moiety. A TON_{Co} of up to 120 was obtained after electrolysis at −0.75 V vs. NHE (−0.34 V vs. RHE) under pH-neutral conditions. However, currents dropped significantly after the first 30 min. The limited stability was again attributed to a loss of the catalyst core from the electrode surface during catalysis.

Cobalt diimine-dioximes can be functionalized on the propanediyl bridgehead of the pseudomacrocyclic equatorial diimine-dioxime ligand. Introduction of anchoring groups to the equatorial ligand enables a substantially more stable integration of the catalyst with the (semi)conducting material

Fig. 12 Chemical structures of cobaloximes and cobalt diimine-dioximes that have been integrated with multi-walled carbon nanotubes for electrocatalytic H₂ evolution from aqueous solutions: pyrene-modified cobaloxime (**31**),⁸⁵ cobaloxime embedded in polymer matrix with pyrene moiety (**32**),⁸⁵ cobaloxime with polymerizable diacetylene unit (**33**),¹³² and a cobalt diimine-dioxime complex (**34**) tethered to multi-walled carbon nanotubes.¹⁶

in comparison to immobilization *via* the axial dative bond in cobaloximes.

The molecular cobalt diimine-dioxime complex **27** (Fig. 10) possesses two phosphonic acid anchoring groups linked to the equatorial diimine-dioxime ligand. These anchoring groups enable strong binding to the surface of metal oxides and the complex was integrated with mesoporous indium tin oxide (ITO) electrodes (ITO/*meso*ITO).⁶⁹ A spectroelectrochemical investigation of the resulting hybrid electrode confirmed a strong anchoring of **27** to the electrode surface in non-aqueous electrolyte, even under reducing conditions in the Co^{II} and Co^I state.^{69,133} Further analyses of the ITO/*meso*ITO/**27** electrode before and after CPE at -0.7 V vs. NHE (-0.29 V vs. RHE) in water (pH 7, TEOA/Na₂SO₄ solution) by XPS, EDX and SEM showed that the molecular complex remained intact, and no decomposition products could be detected. H₂ evolution with a TON_{Co} of 12 and a FE of 87% was confirmed after extended electrolysis at -0.7 V vs. NHE (-0.29 V vs. RHE).⁶⁹

An azide-functionalized cobalt diimine-dioxime complex was covalently attached to a modified CNT electrode *via* click chemistry (**34**, Fig. 12).¹⁶ A high TON_{Co} of 55,000 and a FE of 97% after 7 h of CPE at -0.59 V vs. RHE in pH 4.5 acetate buffer were reported. XPS and cyclic voltammetry measurements after electrocatalysis confirmed integrity of the grafted molecular catalyst on the CNT surface, which once more emphasized the good stability of anchoring *via* the propanediyl bridgehead and of the core ligand itself.

3.2. Cobalt oximes on photocathodes

Hybrid photocathodes based on p-GaP and a cobaloxime complex were constructed by polymerization of vinyl-pyridine or *N*-vinyl-imidazole on the HF-etched surface of the semiconductor, followed by introduction of the cobaloxime core (**35** and **36**, respectively, Fig. 13).^{134–137} Photocurrents between -0.9 and -2.7 mA cm⁻² (0.0 V vs. RHE) were achieved,¹³⁵ and H₂ evolution from pH-neutral aqueous solution (pH 7 phosphate solution) was confirmed with up to near-unity efficiencies after solar light irradiation (100 mW cm⁻²) at 0.0 V vs. RHE.^{134,136} Exchanging the oxime-hydrogen with BF₂ improves the stability, and allowed for operation of the photocathode under more acidic conditions (pH 4.5 acetate buffer), where the H-bridged cobaloximes are unstable.¹³⁸ Under these conditions, a maximum photocurrent of -1.1 mA cm⁻² and a FE of 97% were achieved at 0.0 and -0.12 V vs. RHE, respectively. In all cases, loss of the cobaloxime core was observed, which most likely limited the long-term performance of the photofunctional constructs.

Anchoring of a carboxylic acid-functionalized cobaloxime

(**3**, R = COOH, Fig. 5) to an ALD-TiO₂-coated p-GaInP₂ electrode (ALD = atomic layer deposition) was described.¹³⁹ In this case, an additional ALD-TiO₂ layer of 0.4 nm thickness was applied on top of the molecular catalyst layer for further stabilization on the electrode surface.¹⁴⁰ Initial cathodic photocurrents of approximately -9 mA cm⁻² and a high TON_{Co} of approximately $1.4 \cdot 10^5$ were reported after 20 h of photoelectrolysis at 0.0 V vs. RHE under 1 sun illumination (100 mW cm⁻²) in pH 13 NaOH solution. These are quite unique conditions for a H₂-evolving molecular catalyst-based hybrid photocathode. It was reported to operate under strongly alkaline conditions, whereas the majority of hybrids requires mildly acidic or neutral conditions to operate with good efficiencies. However, even though XPS data have been reported showing that some cobalt remains on the electrode surface, the integrity and stability of the cobaloxime catalyst requires further investigation under the employed extreme conditions.^{79,104,141}

Cobaloximes have also been integrated with dye-sensitized p-type NiO electrodes. The complexes were either incorporated *via* a supramolecular assembly (**37**, Fig. 13),¹⁴² or co-immobilized with a molecular photosensitizer (**29** or **40**) on the NiO surface (complexes **38** and **39**, Fig. 13).^{12,131} Photocurrents between -13 and -44 μ A cm⁻² (0.0–0.2 V vs. RHE) were achieved, and H₂ was produced with up to 68% FE in case of the hybrid photocathodes using **37** and **39**. A higher photocurrent of -110 μ A cm⁻² and a FE of 81% were obtained when using a CdSe QD-sensitized NiO electrode with complex **26** as catalyst (Fig. 10).¹⁴³ Overall, these studies do not consider the inherently labile Co-pyridine bond when drawing conclusions on the stability of the photocathode.

Fig. 13 Chemical structures of cobaloximes (**35–39**) used in photoelectrocatalytic hybrid devices for H₂ evolution. The complexes were integrated with p-GaP (**35** and **36**), or dye-sensitized NiO (**37–40** in combination with dye **29** or **40**).

Photoelectrochemical H₂ evolution with cobalt diimine-dioxime complexes has also been reported. An azide-functionalized complex was linked to an organic dye (**41** and **42**, Fig. 14),^{129,144} or a C₆₀ fullerene derivative (**43**, Fig. 14)¹⁴⁵ *via* click chemistry, and then further grafted onto a

p-type NiO electrode or an organic PV-inspired photocathode, respectively. For the photocathode constructed by NiO and **41**, photocurrents of up to $-15 \mu\text{A cm}^{-2}$ were observed at 0.14 V vs. RHE under visible light irradiation ($\lambda = 400\text{--}800 \text{ nm}$, 65 mW cm^{-2}) in aqueous pH 5.5 MES/NaCl buffer solution, and the construct evolved H₂ with approximately 9% FE.¹²⁹ Initial photocurrents of -0.2 to -0.3 mA cm^{-2} were observed in pH 4.8 acetate and pH 6.8 phosphate buffer solution for the NiO-**42** hybrid photocathode, which then stabilized at approximately $-10 \mu\text{A cm}^{-2}$ after about 10 minutes at 0.46 V and 0.60 V vs. RHE, respectively (white LED, 17 W).¹⁴⁴ Only traces of H₂ were detected qualitatively, and the TON was far below 1. The low efficiency and activity are in line with other reports using dye-sensitized NiO as photocathode,¹²⁸ and it was assigned to reductive degradation of NiO as well as potential catalyst and dye decomposition.

In the case of the organic photocathode, the C₆₀ derivative was chosen as anchor for the cobalt diimine-dioxime (**43**) based on its good interaction with the organic light-absorbing part (organic polymer) of the electrode, and its capability to function as an electron extraction layer guiding electrons from the light-absorber to the catalyst.¹⁴⁵ For this assembly, only small photocurrents ($-2 \mu\text{A cm}^{-2}$) were observed under 1 sun irradiation (100 mW cm^{-2}) at 0.0 V vs. RHE in pH 4.5 acetate buffer. Detection of H₂ was not reported.¹⁴⁵

The cobalt diimine-dioxime complex **28** (Fig. 10) was integrated with TiO₂-protected p-Si electrodes.¹⁴⁶ A mesoporous TiO₂ coating was introduced to the flat p-Si electrode after etching to protect it from passivation, and to aid electron transfer from the light-absorber to the catalyst. In addition, the mesoporosity enabled high loadings of the molecular catalyst compared to the flat p-Si surface. With **28**, a photocurrent of approximately $-340 \mu\text{A cm}^{-2}$ was achieved at 0.0 V vs. RHE under 1 sun illumination ($\lambda > 400 \text{ nm}$, 100 mW cm^{-2}) in pH 4.5 acetate buffer solution. H₂ was produced in prolonged photoelectrolysis experiments, giving a TON_{Co}

of 10.5 ± 0.5 after 4 h, which is similar to the TON_{Co} obtained in photocatalytic particle systems (DSP).²⁶

4. Conclusions and outlook

Cobalt oxime complexes are among the best-studied molecular proton reduction catalysts, including catalytic mechanism and structure-activity relationships. Their outstanding properties have evoked their usage in a variety of different electro- and photo(electro)catalytic schemes that are the focus of this review. They are often used as first-choice catalyst when introducing new concepts for the catalytic reduction of H₂. Their simple synthesis allows for easy introduction of a large number of different functional groups for surface modification in PEC and DSP systems. The profound knowledge on catalyst behavior aids to analyze the new systems, and obtain a fundamental understanding of the hybrid materials before extending the application of the concepts to less well-studied catalysts, or even new types of proton reduction catalysts.

The incorporation of the catalyst into polymer scaffolds, or *via* the robust equatorial ligand was shown to significantly improve the stability of the cobalt oxime catalyst in a hybrid device. However, long-term stability of such systems is still limited to a couple of days due to degradation of the organic oxime ligand. Strategies to improve the longevity could involve further enhancement of the catalytic rate to successfully compete against side reactions such as hydrogenation.

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6. References

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Fig. 14 Chemical structures of cobalt diimine-dioximes (**41–43**) used in photoelectrocatalytic hybrid devices for H₂ evolution. The complexes were integrated with NiO (**41** and **42**) *via* an organic dye, or anchored to an organic photocathode (**43**).

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Profile

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