

Light-Driven Hydrogen Generation: Efficient Iron-Based Water Reduction Catalysts**

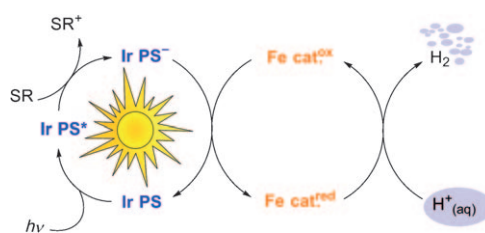
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Hydrogen is considered to be an attractive energy source, since it can be used in a clean and highly efficient manner in fuel cells. A current drawback for the wider use of hydrogen is the dependence of hydrogen production on fossil resources by reforming processes. Obviously, a more benign objective is the conversion of the almost unlimitedly available energy of sunlight into non-fossil-based energy carriers such as hydrogen using water as the hydrogen source.

Since the discovery of the Honda Fujishima effect in 1972,^[1] photocatalytic water splitting into hydrogen and oxygen has inspired researchers all over the world to develop novel and economical photocatalysts for this reaction.^[2] In the past, mainly heterogeneous materials were developed for the photocatalytic water splitting into H₂ and O₂, but only a few homogeneous systems have been reported for this reaction to date.^[3] The lack of activity in homogenous systems is related to the complexity of the multielectron processes during water reduction (two electrons per molecule H₂) and water oxidation (four electrons per molecule O₂). To improve the overall process, the two half reactions water oxidation and water reduction can be studied separately employing sacrificial reagents (SR) that donate (water reduction)^[4] or accept (water oxidation) electrons in the catalytic system. For water oxidation cerium(IV) reagents are often used, and remarkable results were reported in the last few years.^[5] In water reduction systems amines such as triethylamine (TEA) or triethanol amine (TEOA) are typically applied as electron donors.

In the late 1970s, the first homogeneous multicomponent systems for water reduction employing photosensitizers (PS) and noble-metal water reduction catalysts (WRC) were established.^[6] The general principle of these water reduction cascades was adapted from nature, where reduction equivalents are generated by light in combination with coupled

redox cycles in photosystems II and I. In such a cascade an iridium PS, for example, is excited by light irradiation and subsequently reductively quenched by the SR to give the reduced species Ir PS⁻. This compound immediately transfers an electron onto the Fe WRC, which then reduces aqueous protons to hydrogen. Thus both the WRC and the PS are required for a catalytic cycle (Scheme 1).



Scheme 1. Principle of the light-driven water reduction cascade with iridium photosensitizer (Ir PS), sacrificial reagent (SR), and an iron water reduction catalyst (WRC).

Beside the original ruthenium(II) bipyridine (bpy) photosensitizers,^[6] notable advancements for PS based on iridium^[7] and platinum^[8] complexes were reported by the groups of Bernhard and Eisenberg, respectively. Moreover, organic dyes such as eosin^[9] have been applied in water reduction catalysis.

With respect to the water reduction catalysts (WRCs), to date most work has focused on noble metals such as rhodium, palladium, or platinum. Hence, in a state-of-the-art water reduction from Bernard and co-workers employing an Ir PS and a Rh WRC, an impressive turnover number (TON) of 5000 was reported.^[7c] Notably, cobalt-based WRCs with different oxime ligands resulted in high TONs up to 2100 in a Pt PS/Co WRC system.^[8a]

To mimic nature more closely, supramolecular devices have been assembled containing both the PS and the WRC part in one molecule, connected by a linker.^[10] However, these so-called dyads are still less active than the multicomponent systems. Furthermore, nature can be a guideline for further catalyst development: iron- and nickel-based hydrogenases catalyze the reduction of protons with up to 9000 molecules of H₂ per second and site.^[11] Considering this fact, surprisingly few examples employing Fe-based WRCs in photocatalytic water reduction are known.^[12] Sun, Åkermar, and co-workers showed that light-driven water reduction is, in principle, possible with iron complexes, although the reported TON(Fe) of 4.3 for a Ru PS/Fe system is low.^[12a] Parallel to our work, a similar system has been further optimized.^[12c]

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[**] This work has been supported by the State of Mecklenburg-Vorpommern, the BMBF, and the DFG (Leibniz prize). F.G. thanks the Fonds der Chemischen Industrie (FCI) for a Kekulé grant.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200905115>.

Recently, an elegant supramolecular device from zinc porphyrins and iron hydrogenase model complexes was used for proton reduction.^[12b] But again, only low catalyst activity was observed (TON(Fe) $\approx$ 4).

Herein, we report an efficient system for homogeneous reduction of aqueous protons to hydrogen consisting of [Ir(bpy)(ppy)₂](PF₆) (ppy: phenyl pyridine) as the PS; iron(0) carbonyl complexes as simple, cheap, readily available, and abundant WRCs; and triethylamine as SR. Clearly, the development of iron-based catalysts as a substitute for noble metals is a major topic in catalysis.^[13] Our initial attempts for more benign WRCs focused on the use of various Co⁰, Co^I, Co^{II}, Fe^I, Fe^{II}, and Fe^{III} precursors. Typically, we allowed the WRC precursor and [Ir(bpy)(ppy)₂](PF₆) to react for 3 h in 10 mL of a THF/TEA/H₂O (8:2:2) solution under xenon light irradiation.^[14a] All tests resulted only in low hydrogen production, and no stable catalytic systems were found (Table 1, entries 1–3). However, in the presence of

Table 1: Investigations of various metal precursors for light-driven hydrogen production from water with [Ir(bpy)(ppy)₂](PF₆) PS.

Entry ^[b]	Metal precursor	V mL ⁻¹ 3 h (15 h)	TON ^[a] WRC 3 h (15 h)	TON ^[a] Ir PS 3 h (15 h)
1 ^[c]	Fe powder	< 1	–	–
2 ^[c]	[{CpFe(CO) ₂ }] ₂	3	13	33
3 ^[c]	[Co ₂ (CO) ₈]	3	12	33
4	[Fe(CO) ₅]	26	114	282
5	[Fe ₂ (CO) ₉]	32	141	347
6	[(cot)Fe(CO) ₃]	30	132	325
7	[Fe ₃ (CO) ₁₂]	30 (47 ^[d])	132 (207 ^[d])	325 (510 ^[d])
8 ^[e]	[Fe ₃ (CO) ₁₂]	17 (45)	75 (198)	184 (488)
9 ^[f]	[Fe ₃ (CO) ₁₂]	11 (32)	48 (141)	119 (347)
10 ^[g]	[Fe ₃ (CO) ₁₂]	< 1	–	–
11 ^[h]	none	< 1	–	–
12 ^[i]	[Fe ₃ (CO) ₁₂]	< 2	–	–

[a] TON = $n(\text{H})/n(\text{WRC or PS})$. [b] Reaction conditions: 18.5 μmol Fe, 7.5 μmol [Ir(bpy)(ppy)₂](PF₆), 10 mL THF/H₂O/TEA (8/2/2), 300 W Xe lamp,^[14a] 25 °C. [c] No more activity after 3 h. [d] No more activity after 6 h. [e] 385 nm cut-off filter was used. [f] 420 nm cut-off filter was used. [g] No Ir PS added. [h] No Fe WRC added. [i] No TEA added.

simple iron(0) carbonyl complexes, the light-driven reduction of aqueous protons took place without addition of any ligand (Table 1, entries 4–9). Control experiments (Table 1, entries 10–12) without the addition of either SR, PS, or WRC clearly demonstrate that all three components are essential in the catalytic system. No hydrogen evolution or only traces were observed when either the sacrificial reagent TEA, the Ir PS, or iron carbonyl was not present in the mixture.

As shown in Table 1, approximately the same activity is obtained for mononuclear [Fe(CO)₅] as for the oligomeric iron carbonyl complexes [Fe₂(CO)₉], [Fe₃(CO)₁₂], and [(cot)-Fe(CO)₃] (cot: cyclooctatetraene; Table 1, entries 4–7). The evolved gas was collected in an automatic burette and analyzed by GC analysis.^[14b] Besides traces of THF, TEA, and CO, only hydrogen was detected.

Next, we investigated the influence of UV irradiation on hydrogen production in the presence of [Fe₃(CO)₁₂]. It is

important to note that the reaction can be driven by only visible light (Table 1, entries 8 and 9). The use of 385 or 420 nm UV cut-off filters^[14] has two main effects. On the one hand, the reaction rate decreases. On the other hand, the lifetime of the catalytic system is prolonged, resulting in approximately the same Fe TON of 200 after 15 h (Table 1, entries 7 and 8). The extension of the stability of the system might be due to less CO dissociation from iron carbonyl, which is known to take place easily in the presence of UV light.

To investigate the scope of the new system, a fixed amount of [Fe₃(CO)₁₂] (10.0 μmol Fe) and varied amounts of Ir PS were used in a set of experiments (Figure 1). With 0.06 equiv-

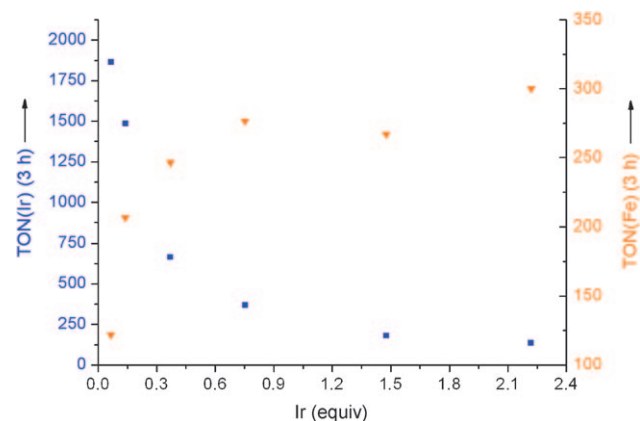


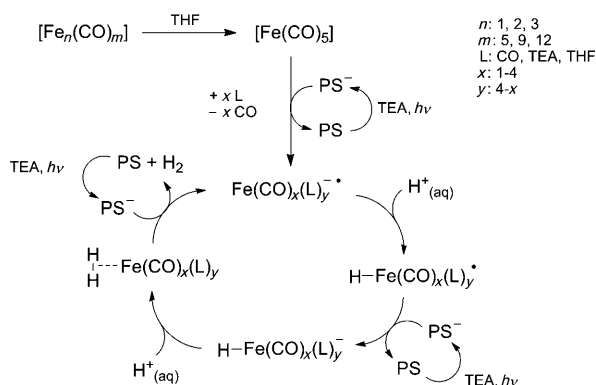
Figure 1. Ir PS TON (blue squares) and Fe WRC TON (orange triangles) with a fixed amount of [Fe₃(CO)₁₂] and varied Ir PS content. Conditions: 10.0 μmol [Fe], 0.06–2.2 equiv [Ir], 10 mL THF/H₂O/TEA (8:2:2), 300 W Xe lamp, no filter, 3 h, 25 °C.

alents Ir PS, the TON for Ir is 1863 after 3 h, and up to 3035 turnovers were observed after 6 h, which are the highest TONs observed. Visible-light irradiation (420 nm cut-off filter) resulted in a TON of 2500 (Ir PS) after 20 h. In an additional set of experiments with fixed amounts of PS (7.5 μmol) and varied amounts of [Fe₃(CO)₁₂] (Figure S2, Supporting Information), a maximum TON of 322 for the Fe WRC without filter and 400 with a 420 nm cut-off filter was obtained with 0.62 equivalents of Fe. These TONs are the best ever reported for an iron WRC system in light-driven water reduction and can compete with the known cobaloxime systems.^[16]

To ensure that the source of liberated hydrogen is water, experiments with D₂O instead of water were carried out. By applying a thermal conductivity detector for gas analysis in GC, we can easily distinguish H₂ and D₂ by the opposite algebraic signs of the integral when helium is used as carrier gas.^[17] Indeed, it was confirmed that water is the only source of hydrogen in the reaction. Furthermore, the necessity of light was demonstrated in an experiment in which any light irradiation on the reaction vessel was excluded in constant time intervals. In the dark gas evolution is interrupted, and it resumes immediately after light is introduced again (Figure S3, Supporting Information).

The mechanism for the photocatalytic proton reduction by iron carbonyl WRCs might be similar to the one proposed by Sun, Åkermark, and co-workers for thiolate-bridged $\text{Fe}^{\text{I}}\text{--}\text{Fe}^{\text{I}}$ dimers.^[12a] The electrochemical properties of $[\text{Fe}(\text{CO})_5]$ and $[\text{Fe}_3(\text{CO})_{12}]$ in THF in the presence and absence of water were investigated previously. It was shown that $[\text{Fe}_3(\text{CO})_{12}]$ degrades to mononuclear $[\text{Fe}(\text{CO})_5]$ and other iron carbonyl compounds in THF solution.^[18] Monomeric $[\text{Fe}(\text{CO})_5]$ shows one reduction peak at -1.8 V versus Ag/AgCl , which is consistent with our own measurements (for electrochemical details, see the Supporting Information). In the same study it was demonstrated that $[\text{HFe}(\text{CO})_4]^-$ could be formed by electrochemical reduction of $[\text{Fe}(\text{CO})_5]$ in a THF/water mixture.^[18]

This scheme can be adapted to the newly developed catalytic system. In the catalytic cycle, electrons for the reduction of the iron WRC are provided by the reduced Ir PS⁻. This species is generated by photoexcitation of Ir PS and subsequent reduction with TEA as SR (Scheme 1, Scheme 2). Thus triethylamine is the final electron source. It



Scheme 2. Proposed mechanism for the reduction of aqueous protons by iron carbonyls and PS.^[12a,19]

has been used before in combination with iridium sensitizers.^[7] The oxidative degradation pathways of tertiary amines have been studied previously, and different radical and cationic species, including the radical $\text{N}(\text{Et})_3^{\cdot+}$, were proposed as the primary reaction product.^[4a,15] From the resulting hydrido iron carbonyl species $[\text{HFe}(\text{CO})_4]^-$ hydrogen is evolved by protonolysis (Scheme 2), which is also postulated for biomimetic hydrogenase models in electrochemical hydrogen production from water.^[12,19]

In conclusion, we have developed a novel, convenient, bimetallic system for water reduction cascades consisting of simple, cheap, and readily available iron(0) carbonyls; TEA as a sacrificial reagent; and an iridium photosensitizer. The activity for the iron water reduction catalyst is the highest for any iron water reduction system known to date and can compete with the known cobaloxime water reduction catalysts.

Experimental Section

All catalytic experiments were carried out under an argon atmosphere with exclusion of air. THF, TEA, and doubly distilled water were degassed with standard laboratory methods prior to use. The catalyst precursors were purchased from commercial suppliers (Aldrich). $[\text{Ir}(\text{bpy})(\text{ppy})_2]\text{PF}_6$ was synthesized according to a literature procedure.^[7c] The amount of gas liberated was measured by an automatic gas burette. Details on the equipment, which is also used for hydrogenation reactions, have been published elsewhere.^[20] In addition, GC for analyzing gases was used (gas chromatograph HP 6890N, carboxen 1000, TCD, external calibration). The light source was a 300 W Xe lamp.^[14]

Typical procedure for light-driven water reduction: A double-walled thermostatically controlled reaction vessel was evacuated and purged with argon five times to remove any other gas. The iridium sensitizer (7.5 μmol) and $[\text{Fe}_3(\text{CO})_{12}]$ (18.5 μmol) were added as powders in a Teflon crucible or as a solution from a freshly prepared stock solution. A solution of THF/ H_2O /TEA (8:2:2, 10 mL) was added, and room temperature was maintained. The reaction was started after stirring at ambient temperature for 8 min by switching on the light source. The variability of gas evolution is typically 1–10%.

Received: September 12, 2009

Published online: November 20, 2009

Keywords: energy conversion · homogeneous catalysis · iron · photochemistry · water splitting

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