



## Copper-based water reduction catalysts for efficient light-driven hydrogen generation



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### ABSTRACT

Although largely neglected, convenient and commercially available copper salts constitute appropriate precursors for efficient and stable water reduction catalysts (WRC). Various copper salts have been applied in the photocatalytic proton reduction together with [Ir(ppy)<sub>2</sub>(bpy)]PF<sub>6</sub> as photosensitizer (PS) and triethylamine (TEA) as electron donor. Among them, copper(I) iodide showed the best productivity, resulting in a TON<sub>Cu</sub> of 260 and a stability of 4 days. The addition of 2,2'-bipyridine (bpy) led to a significant improvement of the catalytic system. Application of 2 equiv. of bpy and an increased amount of PS improved the stability as well as the productivity (TON<sub>Cu</sub> 711). Remarkably, this catalytic system was reactivated seven times with only further addition of fresh PS and TEA. Consequently, this copper-based WRC was shown to be active for more than 48 days reaching a maximum TON<sub>Cu</sub> of >3900, which is in the same order of magnitude as previously known noble metal WRCs. Aberration-corrected HAADF-STEM measurements revealed a part transformation of the molecularly-defined copper precursor into Cu containing nanoparticles of 5–10 nm size. Additionally, by XAS measurements the conversion of the copper(I) salts into Cu(0) compounds under light irradiation was observed. With respect to low costs and high abundance of copper these WRCs are an appropriate alternative for noble metal based catalysts.

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### 1. Introduction

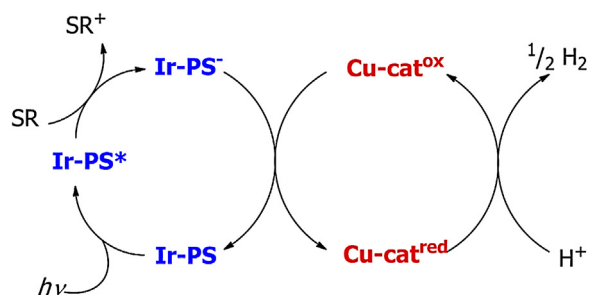
Renewable energies such as wind and sunlight contribute progressively to a sufficient and sustainable energy supply [1]. However, due to its fluctuating occurrence, the storage of electric energy becomes increasingly important. In this respect, various approaches for the interconversion of electric and chemical energy, e.g. by power to gas methods, are currently discussed. Here, hydrogen is of particular interest as a secondary energy carrier [1]. Hence, its generation from suitable starting materials, especially water, its storage and conversion back to electrical energy is a current topic of intensive research [1,2]. In fact, an increasing number of pilot plants combining wind mills or photovoltaic devices with classical

water electrolysis are installed worldwide. Compared to the latter combination, possessing an overall efficiency between 10 and 14% [3], a more efficient way for the conversion of the sun's energy to hydrogen is desirable [4,5]. A possible solution would be the direct photocatalytic water splitting into hydrogen and oxygen. To improve the overall water splitting process, typically the two half reactions (water oxidation and water reduction) are studied separately employing sacrificial reagents as electron donors or electron acceptors [5,6]. In order to develop improved catalysts for this application, a general trend towards the usage of 3d metals is evident. Such catalysts would be of special advantage due to costs, abundance and toxicity compared to noble metals. Thus, significant efforts have been reported applying iron, cobalt and nickel complexes as water reduction catalysts (WRC) in the photocatalytic hydrogen generation from water [7]. Unfortunately, all these catalysts are either deactivated within a few days or require a huge excess of additional ligands to be stabilized. Molecularly-defined copper compounds have been largely neglected in photocatalytic water splitting despite their ability to act as catalysts for

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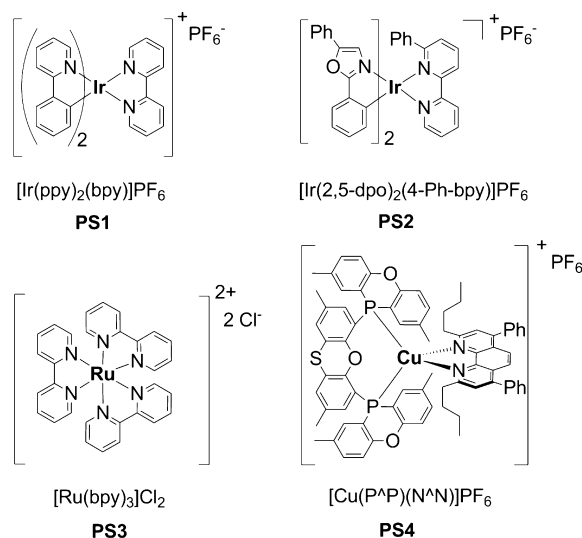
**Scheme 1.** The basic concept of hydrogen generation from water by application of an Ir-photosensitizer (PS) and a copper-based water reduction catalyst (WRC) in the presence of the sacrificial reductant triethylamine (SR).

electrochemical water oxidation [8] and CO<sub>2</sub> reduction [9]. On the other hand, heterogeneous cupric and cuprous oxides have been used as co-catalysts, mainly supported on titania [10], or as light harvesting semiconductors [11] for water reduction. Recently, homo- and heteroleptic copper complexes proved to be appropriate photosensitizers for the photocatalytic hydrogen production [12]. In addition, copper(I) polypyridine complexes showed interesting emission properties and therefore are considered as active components in organic light-emitting diodes (OLEDs), light-emitting electrochemical cells (LECs) or luminescence-based sensors [13].

As an extension of our previous work, we report herein the application of various copper salts as proton reduction catalysts for photocatalytic water splitting (Scheme 1). Interestingly, these molecularly-defined precursors are partly transformed during the water reduction reaction into highly active and stable nanoparticles. Consequently, this study contributes to the development of convenient and abundant copper WRCs and provides a deeper insight into their mode of operation.

## 2. Results and discussion

Initially, we tested various copper(I) and copper(II) compounds as WRC with [Ir(ppy)<sub>2</sub>(bpy)]PF<sub>6</sub> as photosensitizer (PS) in a THF/H<sub>2</sub>O mixture in the presence of triethylamine (SR = sacrificial reductant) (Table 1) [14]. Based on our previous experience regarding the influence of different ratios of THF, TEA and water the optimal conditions applying the same Ir-PS together with Fe<sub>3</sub>(CO)<sub>12</sub> as WRC were chosen [15]. Our actual investigations included simple and commercially available copper salts as well as four different photosensitizers. Several copper(I) and copper (II) salts like triflate, acetate, chloride and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> showed a limited activity in the range of 30–55 turnovers after 3 h (Table 1, entries 1–6). It is noteworthy to mention that a number of catalysts are deactivated after 6–8 h. Remarkably, only copper(I) iodide yielded a TON of more than 100 after 3 h (Table 1, entry 7). Both, copper(I) and copper(II) compounds were active in the water reduction. Using copper(II) acetate as precursor the TON was almost twice as high as for copper(I) acetate after 3 h (Table 1, entries 3 and 4). However, no influence of the initial copper oxidation state onto the activity could be observed in the case of chloride salts (Table 1, entries 5 and 6). Due to the reducing conditions applied here, a conversion of copper(II) into copper(I) cannot be excluded. Additionally, the influence of the iodide counter ion on the activity was exemplarily studied according to the high activity of copper iodide (Table 1, entry 7). While the addition of an iodide source (*i.e.* KI) to copper(II) acetate initially had a detrimental effect, for copper(II) triflate an increase of the TON by a factor of 1.4 after 3 h and 1.7 after 20 h, respectively, was observed (Table 1, entries 8 and 9). However, the productivity of CuI could not be achieved. For comparison, also commercially available copper oxides and Cu core/CuO shell nanoparticles were tested. These samples resulted



**Fig. 1.** Structures of the photosensitizers PS1–4 applied in the water reduction according to Table 1 (ppy = 2-phenylpyridine, bpy = 2,2'-bipyridine, 2,5-dpo = 2,5-diphenyloxazole) [17].

in poor to medium productivities (Table 1, entries 10–13). Among them, the best result was achieved with CuO nanoparticles (Table 1, entry 12 and Fig. S2-1), reaching approximately 30% of the TON of CuI. The higher activity of CuI is most likely due to the lower reduction potential of CuI (0.00 V vs. SHE) for CuI<sub>2</sub><sup>-</sup> + e<sup>-</sup> → Cu + 2 I<sup>-</sup> compared to 0.521 V for Cu<sup>+</sup> + e<sup>-</sup> → Cu [16].

On the basis of these results we chose CuI for further experiments. First, we tested other photosensitizers which had shown good performances in our previous investigations (Fig. 1) [6a–c, 12c and d]. Among them the [Ir(2,5-dpo)<sub>2</sub>(4-Ph-bpy)]PF<sub>6</sub> (PS2) gave the best result, almost comparable to [Ir(ppy)<sub>2</sub>(bpy)]PF<sub>6</sub> (Table 1, entry 14). Application of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (PS3) resulted in no hydrogen evolution (Table 1, entry 15). [Cu(2,9-di-*n*-butyl-4,7-diphenyl-1,10-phenanthroline) (10,10'-(2,8-dimethyl-phen-oxathiine-4,6-diyl)bis(2,8-dimethyl-10Hphen-oxaphos-phinine))]PF<sub>6</sub> (PS4) deactivated already after 3 h (Table 1, entry 16). Working without a cut-off filter caused almost the same initial activities. However, a faster deactivation was observed. Whereas application of a 420 nm cut-off filter significantly decreased the catalytic performance. This can be explained by the removal of the most relevant wavelengths for the excitation of PS1 from the light beam (Table 1, entries 7, 17 and 18; UV-vis spectrum of PS1 in Fig. S3). Additionally, it was shown that both, the PS as well as the WRC, were essential to drive the reaction (Table 1, entries 19 and 20). Solely, the Ir-PS1 alone showed some minimal activity which levelled off after 18 h.

Interestingly, the performance of the photocatalytic system was significantly improved by the addition of organic ligands. Therefore, various mono- and multidentate nitrogen as well as phosphorous containing ligands were tested (Table 2). The reaction time has been elongated up to 96 h, since the positive influence of ligands is expected to improve especially the long-term stability of the overall system. Within 96 h a TON of 260 has been achieved with PS1 and CuI in the absence of any additional ligand (Table 2, entry 1). While the addition of 2 equiv. of either triphenylphosphine (PPh<sub>3</sub>), bis(diphenylphosphino)ethane (dppe), 1,10-phenanthroline (phen), pyridine or bathocuproinedisulfonic acid disodium salt (BC(SO<sub>3</sub>Na)<sub>2</sub>), resulted in less stable systems (Table 2, entries 2, 3, 5, 6 and 10), *N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>2</sup>,*N*<sup>2</sup>-tetramethylethane-1,2-diamine (tmEDA, 2 equiv.), 3 equiv. of pyridine and 2,2':6,2''-terpyridine (tpy, 2 equiv.) led to almost same activities after 20 h as observed without additional ligand present

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