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Iron polypyridyl catalysts assembled on metal oxide semiconductors for photocatalytic hydrogen generation†

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A series of Fe(III) complexes was recently reported that are active for photocatalytic hydrogen generation when paired with fluorescein and triethylamine. Herein we report an Fe(III) complex immobilized on TiO₂ and SrTiO₃ that is significantly more active than the homogeneous system, achieving up to 7800 turnovers in 31 hours.

Harnessing solar energy to split water into hydrogen and oxygen can be achieved through a process called “artificial photosynthesis” (AP).¹ Focusing on the reductive side of AP, solar hydrogen generation is a renewable method to meet the global hydrogen demand.¹ Many transition metal complexes have been shown to be active electrocatalysts for hydrogen generation.² Although many of these complexes are only active in organic solutions, it is important to develop hydrogen generation catalysts that are stable and active in aqueous solutions.² For wide-spread applications, it is increasingly important to make catalytic materials that are made from inexpensive materials.³ To this end, we have recently reported a series of iron polypyridyl monophenolate complexes that are active for hydrogen generation in aqueous solutions.⁴ These iron complexes are made from inexpensive ligand precursors in good yield and are electronically tunable, with overpotentials ranging from 300–800 mV.⁴ With electrocatalysts in hand, one method of developing a photocatalytic system involves combining an electrocatalyst with a chromophore and a sacrificial source of electrons.⁵

Recently, we reported a series of Fe(III) complexes (Fig. 1) that evolve hydrogen when paired with fluorescein (chromophore) and triethylamine (sacrificial donor) in 1:1 ethanol:water mixtures.⁶ This photocatalytic system is highly active and stable, achieving TONs with respect to catalyst (TON_{WRC}) of > 2100 after 24 hours of irradiation. Catalysis was found to proceed through a reductive quenching pathway and continued for over 24 hours

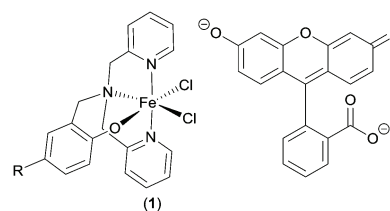


Fig. 1 Left: Iron polypyridyl monophenolate catalyst (1). Right: Fluorescein.

with the addition of more sacrificial donor. Furthermore, this system was robust and catalysis was observed when using local pond water.⁶ Although highly active, hydrogen evolution is still limited by diffusion in homogeneous systems. We reasoned that immobilization of these robust and active polypyridyl monophenolate catalysts on wide-band-gap semiconductors (3.0 eV for rutile TiO₂, and 3.2 eV for anatase TiO₂ and SrTiO₃) would improve activity and potentially allow for recycling of the catalysts. Herein we report the immobilization of an iron polypyridyl monophenolate complex on SrTiO₃ and TiO₂ through a robust phosphonic acid anchoring group. The resulting heterogeneous systems are much more active, achieving turnovers of up to 7800 WRC over 31 hours compared to 2100 for the previously reported homogeneous system.

In order to attach the iron polypyridyl monophenolate catalysts to metal oxide semiconductors, a ligand was designed that contains both the polypyridyl ligand and a pendant phosphonic acid anchoring group for attachment to the metal oxide (Fig. 2). The phosphonate functional group was chosen due to the ability of the linkage to resist detachment in aqueous solutions while allowing for the injection of electrons into the

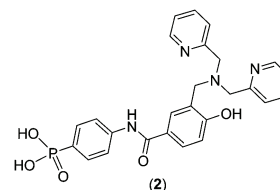


Fig. 2 Phosphonic acid functionalized ligand.

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conduction band of the semiconductor.⁷ Ligand **2** is obtained through amide bond formation between a carboxylic acid derivative of the polypyridyl monophenolate ligand and an amino-derivatized phosphonic ester. The phosphonic ester is then deprotected with TMSBr to afford the ligand in good yield (42%). Synthesis and isolation of an iron complex containing **2** was not possible due to binding of the phosphonic acid group to the vacant sites on the iron catalyst. Attempts at coordinating a protected version of **2** to iron followed by deprotection chemistry yielded similarly unsuccessful results.

In order to circumvent these synthetic difficulties, we reasoned that the complex could be assembled on the surface of the metal oxide semiconductor. When the metal oxide was sensitized with **2**, the phosphonic acid bound preferentially to the semiconductor, leaving the polypyridyl monophenolate available to bind to iron. More specifically, metal oxide nanoparticles were stirred in a solution of excess **2** in methanol for 1 hour. The resulting nanoparticles were centrifuged and the excess solution was removed. These nanoparticles were then rinsed several times with methanol. **2**-TiO₂ and **2**-SrTiO₃ were then suspended in a methanolic solution of FeCl₃ to yield the immobilized catalyst (Fig. 3).

Upon assembly, the sensitized TiO₂ appears purple, with a strong absorbance at $\lambda_{\text{max}} = 515$ nm in the diffuse reflectance UV-Vis spectrum. This absorbance corresponds to the $p\pi-d\pi^*$ transition from the phenolate to the Fe(III) center that is observed in the parent complex (**1**), suggesting that the iron complex has formed (Fig. 4). Interestingly, when bare TiO₂ (not sensitized with **2**) is exposed to FeCl₃, no significant visible absorbance is observed (see ESI†). ATR-IR was also used to confirm phosphonate binding to the metal oxides (see ESI†). Similar characterization techniques were used to confirm catalyst formation on SrTiO₃.

Owing to the success of fluorescein as a chromophore in the previously reported homogeneous system, we examined its use when paired with the catalyst sensitized metal oxides. Gratifyingly, fluorescein forms aggregates on the surface of TiO₂ and SrTiO₃ (see ESI†). When TiO₂ and SrTiO₃ are treated with a solution of fluorescein in ethanol, the resulting nanoparticles exhibit a strong absorbance at $\lambda_{\text{max}} = 500$ nm (see ESI†), suggesting aggregation

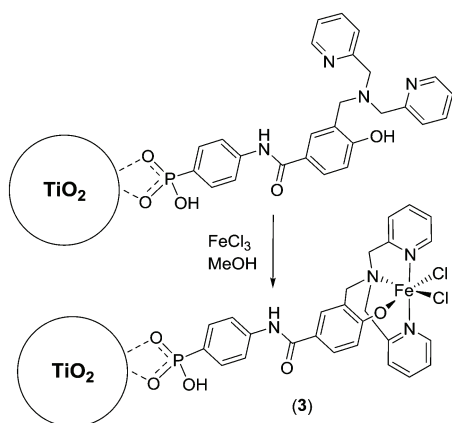


Fig. 3 Assembly of iron catalyst (**3**) on TiO₂.

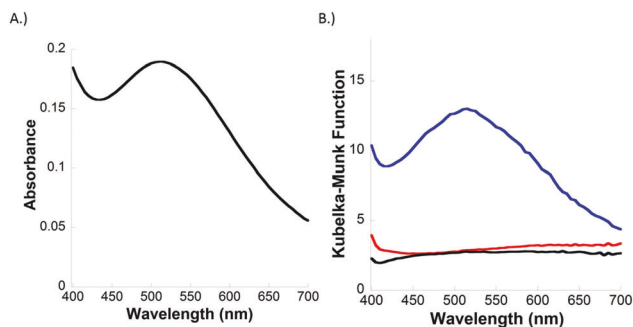


Fig. 4 (A) UV-Vis spectrum of homogeneous iron catalyst **1** where R = H. (B) Diffuse-reflectance UV-Vis spectra of bare TiO₂ (black), **2**-TiO₂ (red), and the assembled iron catalyst (**3**-TiO₂, blue).

of fluorescein on the surface. Aggregation of structurally similar rhodamine dyes and electron injection from these aggregates have been observed on TiO₂.⁸

With aggregation observed for fluorescein on metal oxide surfaces, catalyst-sensitized nanoparticles were combined with a solution of 2 mM fluorescein and 5% triethylamine in 1:1 ethanol:water. Upon irradiation with green light-emitting diodes ($\lambda = 520$ nm, 0.12 W), hydrogen evolution was observed for solutions containing FI, catalyst-sensitized metal oxide, and TEA (Fig. 5). The optimal fluorescein concentration was found to be 2.0 mM, with an optimal pH for the solution at 12.5 (see ESI†). This is consistent with other photocatalytic systems containing this chromophore and sacrificial donor.⁹ FI is also known to decompose at pH < 12.5 upon photolysis.⁹ Minimal hydrogen was observed from irradiation of the solution of bare metal oxide, and no hydrogen was observed in the absence of fluorescein (see ESI†).

Interestingly, both **3**-TiO₂ and **3**-SrTiO₃ are highly active for hydrogen generation in a 2.0 mM solution of fluorescein with 5% TEA (Fig. 5 and Table 1). Owing to the high overpotential

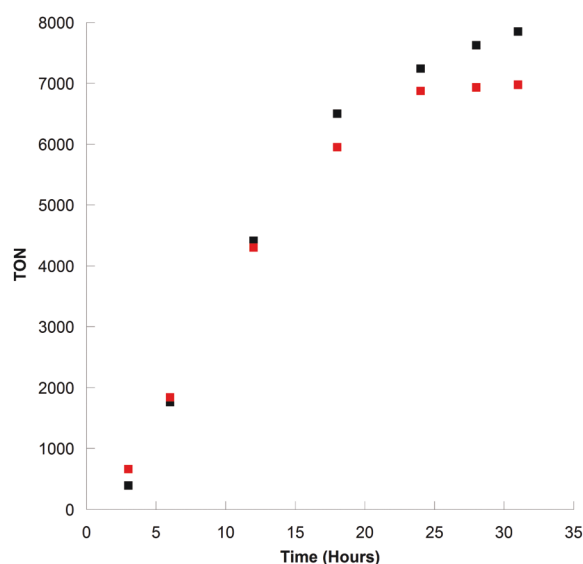


Fig. 5 Hydrogen generation from **3**-TiO₂ (black) and **3**-SrTiO₃ (red) with 2 mM fluorescein and 5% TEA in 1:1 ethanol:water.

Table 1 Solutions of 1 mg catalyst sensitized metal oxides, 2 mM fluorescein, 5% TEA in 1 : 1 ethanol : water after 31 hours irradiation

Nanoparticle description	H ₂ generated (μL)	TON
3-SrTiO ₃	2660	7000
3-TiO ₂	2900	7800
3-ZrO ₂	12	7

(800 mV) of **1** for electrocatalytic proton reduction, it was of interest to investigate the use of SrTiO₃. SrTiO₃ has a band gap of 3.2 eV and has a flat band potential that is more negative than TiO₂.¹⁰ The samples containing 3-SrTiO₃ (Fig. 5, red) were initially more active than 3-TiO₂ (Fig. 5, black). However, after 10 hours of irradiation, the activity of 3-SrTiO₃ began to slow, resulting in 7000 TONs after 31 hours of irradiation. The apparent cessation of hydrogen evolution for 3-SrTiO₃ is likely due to faster chromophore decomposition on the surface. The system containing 3-TiO₂ was more stable than 3-SrTiO₃, achieving 7800 TONs after 31 hours of irradiation. Hydrogen generation ceases after 31 h for 3-TiO₂.

Gratifyingly, once hydrogen generation ceases, the catalyst-sensitized nanoparticles can be collected and rinsed. When these nanoparticles are combined with fresh chromophore and sacrificial donor, hydrogen generation continues at the same initial rate (see ESI†). This suggests that chromophore and donor decomposition is likely the reason for the cessation of hydrogen generation.

In order to test whether electron injection from the chromophore into the conduction band of the metal oxide plays a role in the observed catalysis, ZrO₂ was examined as a non-injecting solid support. Catalyst formation on the surface of ZrO₂ was observed using diffuse reflectance UV-Vis (see ESI†). However, upon irradiation, catalyst-sensitized zirconia did not generate significant hydrogen (Table 1). This suggests that electron injection from fluorescein into the conduction band of SrTiO₃ and TiO₂, followed by the reduction of surface bound catalysts likely plays a role in catalysis.

Additional control experiments were also performed to probe whether the surface assembled catalyst is the active species generating hydrogen. When SrTiO₃ and TiO₂ were treated with FeCl₃ with no ligand present, only 80 μL and 200 μL of hydrogen were generated after 24 hours of irradiation, respectively. Bare SrTiO₃ and Bare TiO₂ produced only 40 μL and 80 μL of hydrogen when combined with 2 mM fluorescein, and 5% TEA in a 1 : 1 water : ethanol mixture, respectively. In each case, the catalyst sensitized metal oxides produced significantly more (> 2500 μL) hydrogen gas.

In summary, we assembled a polypyridyl monophenolate iron catalyst on the surface of metal oxides through a robust phosphonic acid linkage. When catalyst-sensitized TiO₂ and SrTiO₃ are irradiated in a solution of 2 mM fluorescein and 5% TEA, the heterogeneous system is several times more active than the previously reported homogeneous system (TON_{WRC} = 7800 after 31 hours). By overcoming the limitations of diffusion in the previously reported homogeneous system, these heterogeneous catalysts represent a step toward developing a device for AP. Furthermore, assembling catalysts on metal oxides in a stepwise fashion by using the semiconductor as a protecting

group is a promising strategy to synthesize catalytic materials. To our knowledge, the iron catalyst-sensitized metal oxides presented in this manuscript are more active than other noble-metal-free systems in which TiO₂ or SrTiO₃ are sensitized with hydrogen evolution catalysts (TON_{WRC} > 7800, compared to TON_{WRC} < 100 in previously reported systems).¹¹

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Conflicts of interest

There are no conflicts of interest to declare.

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