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Iron Polypyridyl Catalysts Assembled on Metal Oxide Semiconductors for Photocatalytic Hydrogen Generation

N. A. Race, W. Zhang, M. E. Screen, B. A. Barden, W. R. McNamara[a]

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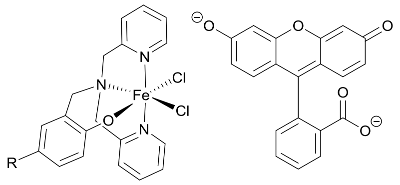
A series of Fe(III) complexes was recently reported that are active for photocatalytic hydrogen generation when paired with fluorescein and triethylamine. Herein we report an Fe(III) complex immobilized on TiO_2 and $SrTiO_3$ that is significantly more active than the homogeneous system, achieving up 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 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 TiO_2, and 3.2 eV for anatase TiO_2 and $SrTiO_3$) would improve activity and potentially allow for recycling of the catalysts. Herein we report the immobilization of an iron polypyridyl monophenolate complex on $SrTiO_3$ and TiO_2 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.



(1)

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

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 conduction band of the semiconductor.[7] Ligand **2** is obtained through amide bond formation between a carboxylic

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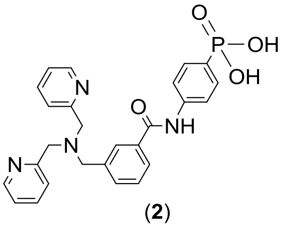
[a] *College of William and Mary, 540 Landrum Drive, Williamsburg, VA 23185*

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x 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 similar unsuccessful results.



(**2**)

Fig. 2. Phosphonic acid functionalized ligand

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**-TiO_2 and **2**-$SrTiO_3$ were then suspended in a methanolic solution of $FeCl_3$ to yield the immobilized catalyst (Fig 3).

Upon assembly, the sensitized TiO_2 appears purple, with a strong absorbance at λ_{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 TiO_2 (not sensitized with **2**) is exposed to $FeCl_3$, no significant visible absorbance is observed (see supporting information). ATR-IR was also used to confirm phosphonate binding to the metal oxides (see supporting information). Similar characterization techniques were used to confirm catalyst formation on $SrTiO_3$.

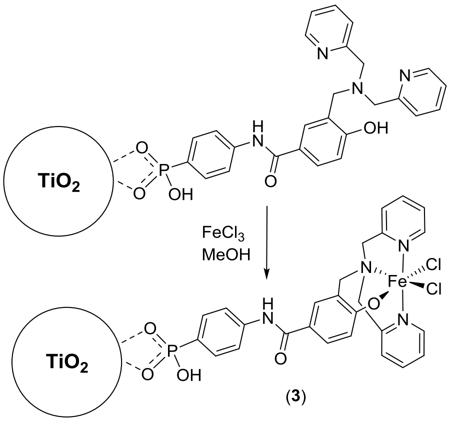


Fig. 3. Assembly of iron catalyst (**3**) on TiO_2.

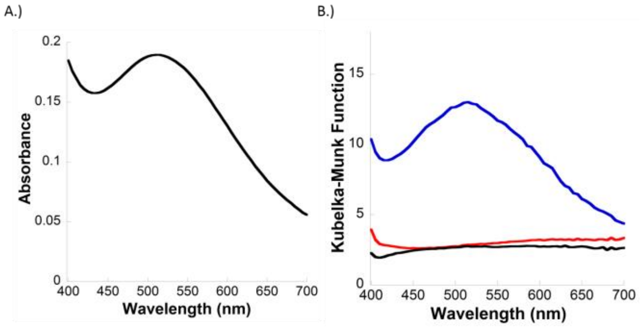


Fig. 4. A) UV-Vis spectrum of homogeneous iron catalyst **1** where R = H. B) Diffuse-Reflectance UV-Vis spectra of bare TiO_2 (black), **2**-TiO_2 (red), and the assembled iron catalyst (**3**-TiO_2, blue).

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 TiO_2 and $SrTiO_3$ (see supporting information). When TiO_2 and $SrTiO_3$ are treated with a solution of fluorescein in ethanol, the resulting nanoparticles exhibit a strong absorbance at λ_{max} = 500 nm (see supporting information), suggesting aggregation of fluorescein on the surface. Aggregation of structurally similar rhodamine dyes and electron injection from these aggregates have been observed on TiO_2.[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

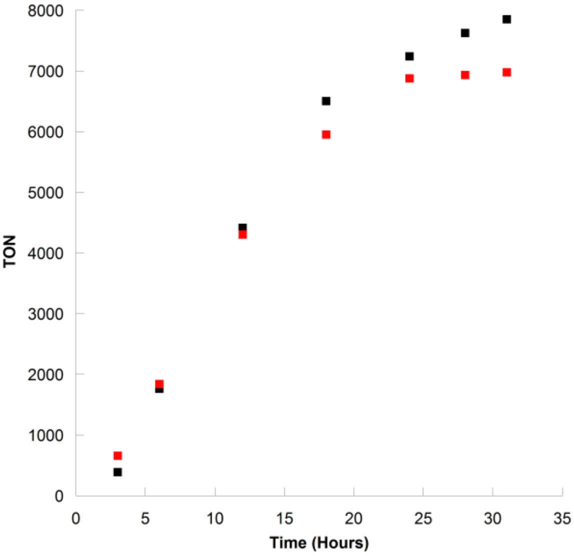


Fig. 5. Hydrogen generation from **3**-TiO_2 (black) and **3**-$SrTiO_3$ (red) with 2 mM fluorescein and 5% TEA in 1:1 ethanol:water.

diodes (λ = 520 nm, 0.12 W), hydrogen evolution was observed for solutions containing Fl, 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 supporting information). This is consistent with other photocatalytic systems containing this chromophore and sacrificial donor.[9] Fl 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 supporting information).

Interestingly, both **3**-TiO_2 and **3**-$SrTiO_3$ are highly active for hydrogen generation in a 2.0 mM solution of fluorescein with 5% TEA (Fig. 5, Table 1). Owing to the high overpotential (800 mV) of **1** for electrocatalytic proton reduction, it was of interest to investigate the use of $SrTiO_3$. $SrTiO_3$ has a band gap of 3.2 eV and has a flat band potential that is more negative than TiO_2.[10] The samples containing **3**-$SrTiO_3$ (Fig. 5, red) were initially more active than **3**-TiO_2 (Fig. 5, black). However, after 10 hours of irradiation, the activity of **3**-$SrTiO_3$ began to slow, resulting in 7000 TONs after 31 hours of irradiation. The apparent cessation of hydrogen evolution for **3**-$SrTiO_3$ is likely due to faster chromophore decomposition on the surface. The system containing **3**-TiO_2 was more stable than **3**-$SrTiO_3$, achieving 7800 TONs after 31 hours of irradiation. Hydrogen generation ceases after 31 h for **3**-TiO_2.

Gratifyingly, once hydrogen generation ceases, the catalyst-sensitized nanoparticles can be collected and rinsed. If these nanoparticles are combined with fresh chromophore and sacrificial donor, hydrogen generation continues at the same initial rate (see supporting information). 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, ZrO_2 was examined as a non-injecting solid support. Catalyst formation on the surface of ZrO_2 was observed using diffuse reflectance UV-Vis (see supporting information). 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 $SrTiO_3$ and TiO_2, followed by the reduction of surface bound catalysts likely plays a role in catalysis.

Nanoparticle Description	H_2 Generated (µL)	TON
3-$SrTiO_3$	2660	7000
3-TiO_2	2900	7800
3-ZrO_2	12	7

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

Additional control experiments were also performed to probe whether the surface assembled catalyst is the active species generating hydrogen. When $SrTiO_3$ and TiO_2 were treated with $FeCl_3$ with no ligand present, only 80 µL and 200 µL of hydrogen were generated after 24 hours of irradiation, respectively. Bare $SrTiO_3$ and Bare TiO_2 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) of 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 TiO_2 and $SrTiO_3$ are irradiated in a solution of 2 mM fluorescein and 5% TEA, the heterogenous 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 TiO_2 or $SrTiO_3$ 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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