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Development of Heterogeneous Photosensitized Transition Metal Oxide Water-Splitting Catalysts on Silica Support

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Running Title: Development of Photosensitized Water Splitting Catalysts

Abstract

The research presented in this manuscript describes the development of photosensitized inexpensive catalysts based on readily available materials. The investigation covers synthesis and characterization of photosensitizers based on porphyrins, mechanical and thermal coating of solid support with semiconducting transition metal oxides, photosensitization of the semiconducting layer, and characterization of the photoelectrochemical properties displayed by the new materials. The process of water oxidation is of primary interest here, with little emphasis put on reduction of protons to gaseous hydrogen. Photoelectrochemically produced protons serve as a probe of effectiveness of the catalysts. Several systems are described, and two catalysts are identified as the most efficient.

Introduction

The photoinduced process of water splitting is currently under heavy investigation by several research groups (O'Regan and Grätzel 1991). There are a number of reasons why there is so much interest in water splitting. For example, because the primary source of energy harvested to power the process (effectively converting it to a technologically useful type) is sunlight, the process is "green" in every aspect; the process is also nearly perfectly environmentally friendly due to the renewability of the materials, carbon emission reduction or, complete elimination and the multiple uses for the products of this seemingly simple reaction, namely: oxygen and especially hydrogen. Since technologies already exist that allow for production of renewable and extremely clean energy from hydrogen, e.g. hydrogen cells, cheap mass production of this excellent fuel is highly desirable (Yilanci et al. 2009). Even though several catalysts were developed to facilitate this process, there are multiple factors that render them unsuitable for scale-up; for example cost, low efficiency, rare materials

used for their production, very high purity required, technological challenges, etc. (Bloor et al. 2014). To target a few of these challenges, the following approach is presented in this paper: the components used are inexpensive and readily available; the process of making the catalysts is simple, quick and requires equipment of minimal complexity. The overall goal was to produce a heterogeneous, granular catalyst based on silica coated with a semiconducting photosensitized transition metal oxide.

Figure 1 schematically represents the underlying mechanisms involved in photocatalyzed water-splitting, occurring on and in a granule of the catalyst. Process "A" in Figure 1 involves: a) absorption of photon(s) by the outside layer, which is the photosensitized part of the semiconductor, b) injection of excited, high energy electrons into the conducting band of the semiconductor from its valence band, facilitated by the photosensitizer, and c) production of electron holes in the semiconductor. This mechanism is coupled with process "B": a) contact between water molecules and the semiconductor surface, b) transfer of electrons from water molecules to electron holes, resulting in water oxidation, c) production of gaseous

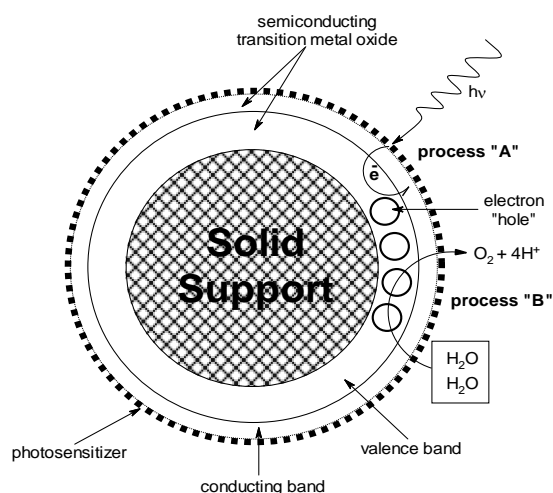


Figure 1. Model of the water splitting mechanisms.

diatomic oxygen and d) production of protons. The increasing proton, or appropriately, hydronium ion concentration quantified over time correlates with efficiency of the system.

The heterogeneous nature of such catalysts offers very high flexibility in coupling of this process and the subsequent (but physically separate) proton reduction, if desired, to gaseous diatomic hydrogen. After a specified low-limit pH is obtained in the light harvesting aqueous suspension, the acidic solution can be filtered and pumped to a complimentary reducing environment in an automated and cyclic mode, returning the catalyst to a fresh batch of neutral water. However, this secondary process is beyond the scope of the current report.

Materials and Methods

The semiconducting metal oxides were purchased from the following suppliers: zirconium dioxide (Alfa Aesar, 99.7%); zinc oxide (Alfa Aesar, 99.999%); titanium dioxide (Loud Wolf LTD, 99.9%); tungsten oxide (Alfa Aesar, 99.998%). Silica 60 (70-230 mesh), pyrrole (98%), propionic acid (99%), zinc acetate dihydrate (97%) were all acquired from Alfa Aesar. Florisil (60-100 mesh) was purchased from J.T. Baker, solvents (reagent grade and better) from Fisher and Macron; *meso*-5,10,15,20-tetrakis-2-carboxyphenyl porphyrin (*o*-TCPP) and *meso*-5,10,15,20-tetrakis-3-carboxyphenyl porphyrin (*m*-TCPP) standards were purchased from Frontier Scientific, and *ortho*-carboxybenzaldehyde and *meta*-carboxybenzaldehyde from ACROS (99%). The lamp used for irradiations was a Bayco 500 W halogen. Measurements were performed with Vernier temperature and pH probes (Logger Pro software) and a Bruker FT-IR ALPHA (Platinum ATR) instrument.

Organic synthesis of photosensitizing dyes was performed according to known methods (Adler et al. 1964, Rothmund 1935, 1936), based on condensation of pyrrole and substituted benzaldehydes in propionic acid as a solvent. Small, pure samples of compounds were acquired as references, from commercial sources.

meso-5,10,15,20-tetrakis-2-carboxyphenylporphyrin: pyrrole (1.688 g, 25.16 mmol) and 2-carboxybenzaldehyde (3.808 g, 17.53 mmol) were mixed with propionic acid (190 mL). The mixture was refluxed for 30 minutes, cooled to room temperature, and then placed in an ice bath for 10 minutes. Filtration and purification (silica column, AcOEt/Hexane/MeOH 75:24:1) yielded the desired free base porphyrins. Figure 2 below schematically shows the method.

Metallation (Zn) of the photosensitizers was performed in order to improve their efficiency according to known methods of metal cation insertion into the porphine core (Kadish et al. 1999); tetraphenylporphyrin, TPP, (300 mg, 0.488 mmol) in CHCl₃ (20 mL) were added to a solution of Zn(OAc)₂•2H₂O (123 mg, 0.560 mmol) and MeOH (3 mL). The reaction reached completion after 3 hours. Completion of the reaction was determined by TLC analysis using a dichloromethane/acetone/acetic acid (8:2:0.1) solvent system. Formation of a new more polar green band signaled completion. This procedure was repeated using pure *ortho*-TCPP (30 mg, 38 μmol) and pure *meta*-TCPP (30 mg, 38 μmol) using a dichloromethane/CHCl₃ (1:1) solvent system. All reactions proceeded in ~quantitative yield as described before (Wang et al. 2005); see Figure 2.

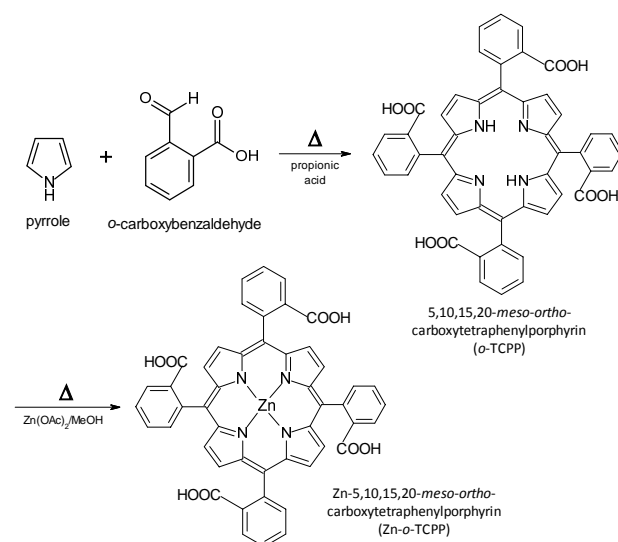


Figure 2. General method of porphyrin synthesis.

Coating and thermal fusion of silica support with semiconducting transition metal oxides was done by vigorous mechanical agitation of silica samples (10 g) with metal oxides (5 g) for 10 minutes, followed by calcination in a furnace for three hours; the oxides used were TiO₂ (450°C), ZnO (350 °C), WO₃ (400°C), ZrO₂ (400°C).

TPP (12 mg, 20 μmol) was added to dichloromethane (20 mL) to make a 0.98x10⁻⁴ M solution. The TPP solution was added to a 100 mg sample of the calcined SiO₂-TiO₂ mixture, with minimal stirring for 60 minutes. The heterogeneous mixture was filtered and dried for 10 minutes. This procedure was repeated for samples of SiO₂-ZnO, SiO₂-WO₃, and SiO₂-ZrO₂.

Development of Photosensitized Water Splitting Catalysts

Zn-TPP (14 mg, 21 μmol) was added to dichloromethane (20 mL) to make a 1.0×10^{-3} M solution. The Zn-TPP solution was added to a 100 mg sample of the calcined $\text{SiO}_2\text{-TiO}_2$ mixture, with minimal stirring for 60 minutes. The solution was filtered and dried for 10 minutes. This procedure was repeated for samples of $\text{SiO}_2\text{-ZnO}$, $\text{SiO}_2\text{-WO}_3$, and $\text{SiO}_2\text{-ZrO}_2$.

Zn-*ortho*-TCPP (16 mg, 19 μmol) was added to dichloromethane (20 mL) to make a 9.3×10^{-4} M solution. The Zn-*ortho*-TCPP solution was added to a 100 mg sample of the calcined $\text{SiO}_2\text{-TiO}_2$ mixture, with minimal stirring for 60 minutes. The solution was filtered and dried for 10 minutes. This procedure was repeated for samples of $\text{SiO}_2\text{-ZnO}$, $\text{SiO}_2\text{-WO}_3$, and $\text{SiO}_2\text{-ZrO}_2$.

Zn-*meta*-TCPP (16 mg, 19 μmol) was added to dichloromethane (20 mL) to make a 9.3×10^{-4} M solution. The Zn-*meta*-TCPP solution was added to a 100 mg sample of the calcined $\text{SiO}_2\text{-TiO}_2$ mixture, with minimal stirring for 60 minutes. The solution was filtered and dried for 10 minutes. This procedure was repeated for samples of $\text{SiO}_2\text{-ZnO}$, $\text{SiO}_2\text{-WO}_3$, and $\text{SiO}_2\text{-ZrO}_2$.

After drying, all samples were then heated on a hot plate at 80 $^\circ\text{C}$ for 10 minutes to allow for complete evaporation of the solvent and adsorption of the porphyrins with the transition metal oxide surface on the silica support.

Measurements

All irradiation trials consisted of a 35 mg sample of the catalysts in 10 mL of deionized water. The solution was placed in a 20 mL beaker with a spin vane. The 500 W halogen lamp was placed 50 cm away from the beaker (non-concentrated light). Over the course of 60 min the pH and temperature of the solution were recorded. Between each trial, the pH probe, temperature probe (thermocouple), beaker and spin vane were thoroughly cleaned.

The temperature monitored during the experiments was not allowed to exceed 42 $^\circ\text{C}$. It was determined experimentally that 50 cm distance between the samples and the lamp was needed to avoid errors in interpretation of oxygen evolution due to the thermally decreased solubility of the gas in water.

The irradiation *controls* consisted of SiO_2 , ZnO, TiO_2 , WO_3 , ZrO_2 , $\text{SiO}_2\text{-ZnO}$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-WO}_3$, $\text{SiO}_2\text{-ZrO}_2$, TPP, ZnTPP, Zn-*ortho*-TCPP, and Zn-*meta*-TCPP.

The irradiation *trials* consisted of $\text{SiO}_2\text{-TiO}_2\text{-TPP}$, $\text{SiO}_2\text{-TiO}_2\text{-Zn-TPP}$, $\text{SiO}_2\text{-TiO}_2\text{-Zn-ortho-TCPP}$, $\text{SiO}_2\text{-TiO}_2\text{-Zn-meta-TCPP}$, $\text{SiO}_2\text{-ZnO-TPP}$, $\text{SiO}_2\text{-ZnO-Zn-TPP}$, $\text{SiO}_2\text{-ZnO-Zn-ortho-TCPP}$, $\text{SiO}_2\text{-ZnO-Zn-meta-TCPP}$, $\text{SiO}_2\text{-WO}_3\text{-TPP}$, $\text{SiO}_2\text{-WO}_3\text{-Zn-TPP}$, $\text{SiO}_2\text{-WO}_3\text{-Zn-ortho-TCPP}$, $\text{SiO}_2\text{-WO}_3\text{-Zn-meta-TCPP}$, $\text{SiO}_2\text{-ZrO}_2\text{-TPP}$, $\text{SiO}_2\text{-ZrO}_2\text{-Zn-TPP}$, $\text{SiO}_2\text{-ZrO}_2\text{-Zn-ortho-TCPP}$, $\text{SiO}_2\text{-ZrO}_2\text{-Zn-meta-TCPP}$.

Please, note that the study did not include proton reduction catalysts in order to make monitoring of the pH drop (increase of the H^+ concentration) possible.

Results and Discussion

The designed photocatalysts performed as expected; a consistent decrease of the pH was observed during the irradiation experiments, accompanied by evolution of oxygen bubbles. TPP was eliminated as a suitable photosensitizer due to the lack of adherence to catalysts' surface. Both: *ortho*-carboxy and *meta*-carboxytetraphenyl porphyrins displayed strong enough binding to the transition metal oxides to efficiently perform their designed function in a stable manner.

Figure 3 shows the representative pH decrease caused by photoirradiation of suspensions of the two most efficient photosensitized catalysts, namely $\text{SiO}_2\text{-TiO}_2$ photosensitized with Zn-*ortho*-TCPP and $\text{SiO}_2\text{-ZrO}_2$ photosensitized with Zn-*meta*-TCPP.

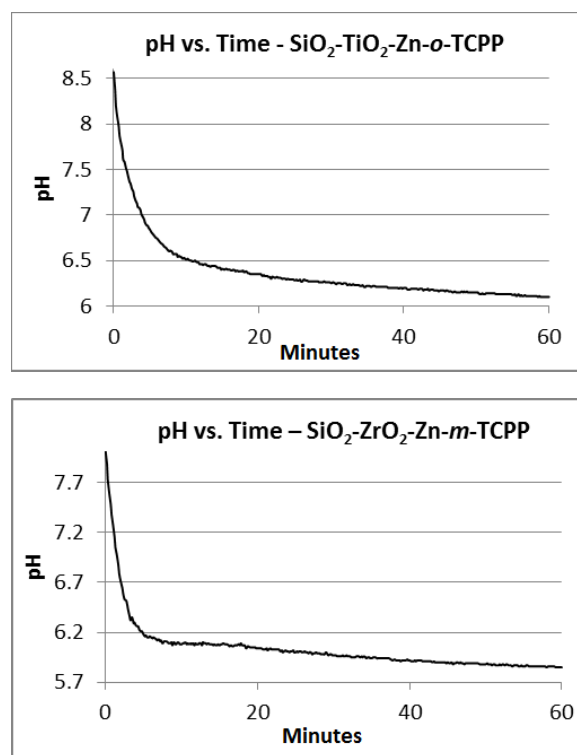


Figure 3. Representative pH decrease caused by photoirradiation facilitated by the two most efficient catalysts.

Table 1. Total change of pH after 60 min of photoirradiation of the tested photosensitizers.

Catalyst	Photosensitizers					
	Zn- <i>o</i> -TCPP			Zn- <i>m</i> -TCPP		
	Initial pH	Final pH	Δ pH	Initial pH	Final pH	Δ pH
SiO ₂ -TiO ₂	8.57	6.1	-2.47	6.69	5.55	-1.14
SiO ₂ -WO ₃	5.94	5.57	-0.37	7.87	7.07	-0.8
SiO ₂ -ZrO ₂	7	5.51	-1.49	8.02	5.85	-2.17
SiO ₂ -ZnO	6.15	6.98	0.83	8.58	7.84	-0.84

A summary of all results is included in Table 1. All control data are available upon request.

Oxygen gas evolution was documented by photographing the irradiated suspensions of the catalysts in DI water. Figure 4 shows the gas bubbles emerging during the process. Quantitative analysis of the gas produced was beyond the scope of this research.



Figure 4. Oxygen bubbles emerging from the photoirradiated heterogeneous mixture: water and SiO₂-TiO₂-Zn-*o*-TCPP.

The least active catalyst was based on tungsten oxide. Catalysts based on zinc oxide and sensitized with Zn-*ortho*-TCPP noticeably *increased* the pH of the solution, presumably due to the formation of zinc hydroxide which dissociates to a very small extent and increases the concentration of hydroxide ions in aqueous solutions.

Conclusions

The most active photocatalysts from the series have been identified and shown to be potential

photocatalytic water-splitting catalysts. The most efficient combinations were titanium oxide sensitized with Zn-*ortho*-TCPP and zirconium oxide sensitized with Zn-*meta*-TCPP. The least active catalyst was based on tungsten oxide; zinc oxide proved to be unsuitable for this application. Future goals include design and investigation of more efficient organic photosensitizers.

Acknowledgements

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