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Control of Electrons’ Spin Eliminates Hydrogen Peroxide Formation During Water Splitting

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ABSTRACT: The production of hydrogen through water splitting in a photoelectrochemical cell suffers from an overpotential that limits the efficiencies. In addition, hydrogen-peroxide formation is identified as a competing process affecting the oxidative stability of photoelectrodes. We impose spin-selectivity by coating the anode with chiral organic semiconductors from helically aggregated dyes as sensitizers; Zn-porphyrins and triarylamines. Hydrogen peroxide formation is dramatically suppressed, while the overall current through the cell, correlating with the water splitting process, is enhanced. Evidence for a strong spin-selection in the chiral semiconductors is presented by magnetic conducting (mc-)AFM measurements, in which chiral and achiral Zn-porphyrins are compared. These findings contribute to our understanding of the underlying mechanism of spin selectivity in multiple electron-transfer reactions and pave the way toward better chiral dye-sensitized photoelectrochemical cells.

INTRODUCTION

Since it has no carbon, has the highest specific enthalpy of combustion of any chemical fuel, and generates water as its oxidation product, hydrogen has been referred to as the fuel of the future. Although significant progress has been made over the past decades, the generation of hydrogen by green, sustainable methods on a global scale remains a future goal. While technologies exist for the electrolysis of water and photoelectrochemical generation of hydrogen from water, the processes involve significant overpotentials and the formation of peroxides and superoxide radical byproducts. These byproducts have the tendency to adsorb onto the photocatalyst, poisoning it, thereby reducing its stability and lifetime. Although specific catalysts are proposed to use the peroxides as intermediates, this path requires higher voltage. Therefore, a fundamental solution for the off-pathway products is essential.

Water splitting is a four-electron process that generates hydrogen molecules having singlet ground states and oxygen molecules having triplet ground states. Commonly, the artificial water splitting process requires an overpotential of about 0.6 V vs normal hydrogen electrode (NHE), to drive the oxygen evolution reaction. The importance of electron-spin correlation of electrons in generating O₂ has been debated for biological photosynthesis. Particularly the chemistry associated with the oxygen evolution reaction in photosystem II has been examined. Nevertheless, the details of the mechanism of the O=O bond formation remain unresolved. Although the spin state of the electrons involved is rarely discussed in works exploring artificial photosynthesis, recent theoretical studies suggest that the overpotential required to split water is linked to restrictions on the electrons’ spin in generating a ground state triplet oxygen molecule. In recent experimental work, it has been shown that when the anode in the water splitting cell is coated with chiral molecules, the overpotential is reduced. It has been proposed that the effect is due to spin filtering occurring when electrons are conducted through chiral systems. However, and very importantly, the possible role of the spin control in suppressing the formation of hydrogen peroxide has not been discussed nor experimentally addressed.

Here, we hypothesize that hydrogen peroxide is produced due to uncontrolled spin alignment and greatly contributes to the high overpotentials. Hence, controlling the spin state of the electronic potential on which the reaction occurs should result in more efficient oxygen production and limited production of hydrogen peroxide. Although we do not strive here to present the highest production of hydrogen and oxygen—optimizing the cells is ongoing—the results presented show an unprecedented control of chemical kinetics through spin selection.

RESULTS AND DISCUSSION

To first control the spin state, the ITO anode in the photoelectrochemical cell was coated with two families of
organic semiconductors, Zn porphyrins and tri(pyrid-2-yl)-amine trisamide, TPyA, both in their chiral (using enantiomerically pure side chains) and achiral (using achiral side chains) versions (Figure 1A,B). By modifying the side chains of the molecules, we control the resulting helical supramolecular assemblies into either a bias for one helical sense or a racemic mixture of both helical senses, respectively. Thus, in the present study, electrons are transmitted into the TiO2 substrate through the same molecular system, which only differs in its molecular organization; either one helical sense or a mixture of both. In the case of Zn-porphyrins, the 390 nm Soret band confirming the formation of helical supramolecular structures in solution (Figure 1C), which are retained when transferred to the surface (inset C). The chiral and achiral TPyA (D and F) their absorption and CD spectra of the aggregated state in solution and when adsorbed on the surface (inset D). The red curves represent the chiral molecules, while the blue represent the achiral ones.

Figure 1. Molecules used as photosensitizer and their supramolecular aggregation. (A) The chiral and achiral Zn porphyrins, (C and E) their absorption spectra and CD spectra of the aggregated state in solution (1.7 × 10−5 M in methylcyclohexane) and when adsorbed on the surface (inset C). (B) the chiral and achiral TPyA, (D and F) their absorption and CD spectra of the aggregated state in solution and when adsorbed on the surface (inset D). The red curves represent the chiral molecules, while the blue represent the achiral ones.

Magnetic conducting atomic force microscopy (mc-AFM) measurements were conducted to verify the spin selectivity of electron transmission through the Zn-porphyrin stacks. Figure 2B shows the dependence of the current on the orientation of the magnetic field at the tip of the mc-AFM for the stack of chiral porphyrins, which confirms that one spin is preferred over the other. It is important to realize that the ratio between the two spin currents is affected by the nonideal spin injection from the magnetic tip. Since the spin polarization of the tip is only about 35%, it means that the actual spin filtering of the molecular system is about 4:1, in other words only about 20% of the electrons conducted through the chiral molecular aggregates in this experiment have the “wrong” spin. From Figure 2C, it can be observed that for the achiral compounds, the magnitude of the current measured as a function of applied bias does not depend on the orientation of the magnetic field; hence the conduction through this system with equal amount of right and left handed helices is not spin specific. These results indicate that the supramolecular structures formed from the chiral porphyrins can efficiently filter spins and are consistent with previous reports in which chiral molecules have been observed to be good spin filters. Next, photoelectrochemical measurements were conducted in a three-electrode cell, with the Ag/AgCl (saturated KCl) as the reference electrode and a Pt wire as the cathode (Figure 3). A 0.1 M Na2SO4 (pH = 6.56) aqueous solution was used as the electrolyte. TiO2 substrates fabricated and functionalized as outlined in the Supporting Information, were used as photoanodes. In these cells, the magnitude of the measured current is correlated with the amount of oxygen bubbles produced at the anode and hydrogen bubbles at the cathode. Higher photocurrent densities are observed for photoelectrodes functionalized with helical aggregates of chiral molecules with preferred helicity, compared to those coated with racemic aggregates of achiral ones. This is remarkable, given that the chemical compositions of the chiral and achiral molecules for the two sets used in this study are very similar, except for the stereocenter present in the chiral molecules. In
general, the magnitude of the photocurrents obtained with the Zn-porphyrins are typically low, as has also been observed by Moore et al. With the TPyA molecules, the photocurrent densities are reasonably high, since UV light is used for illumination of the cell. The activity of the photoelectrodes is known to depend strongly on their electronic properties, therefore Mott–Schottky measurements were performed to characterize the electronic properties of TiO₂ electrodes modified with aggregates of Zn porphyrin and TPyA molecules.

A flat-band potential, $V_{fb}$ of $-0.51$ V vs Ag/AgCl was obtained in the dark for both the chiral and the achiral Zn-porphyrins (Figure 3E), while a value of approximately $-0.70$ V vs Ag/AgCl was obtained for the TPyA molecules (Figure 3F), an indication that the difference in the photocurrents, for chiral and achiral species, is not related to the modification of the electronic properties of the photoelectrodes. Thus, the differences in the photocurrents must be attributed to the chirality of the molecules.

After showing the difference in water splitting for the chiral versus racemic aggregates, the beneficial effect of electrons’ spin control is highlighted by its effect on hydrogen peroxide formation. An indirect quantification of the H₂O₂ produced during photoelectrochemical water splitting was conducted. Spectrophotometric titration of the used electrolytes were performed using o-tolidine as redox indicator. The amount of peroxide formed has been quantified through Ellms-Hauser method calibrating the system with commercial H₂O₂ (see Figures S12–S14). In the presence of H₂O₂, a yellow color appears with an absorption peak at about 436 nm. This peak is characteristic for the complete two-electron oxidation product of o-tolidine formed by the reaction with hydrogen peroxide.

The electrolyte obtained from the bare TiO₂ and electrodes functionalized with achiral dyes showed the characteristic peak at 436 nm, indicating the production of H₂O₂ during water oxidation (see Table S1). Fascinatingly, no detectable amount of hydrogen peroxide was observed for electrodes with the chiral molecules physisorbed (Figure 4A,B). Noticeably, after...
40 min of irradiation, 43 ± 5 mmolL⁻¹ of hydrogen peroxide have been observed for some oxides, 35 induced spin polarization. Of course, the substrate (the catalyst) may make another counterintuitive approach is presented. The TPyA functionalized system while nondetectable levels of peroxide have been produced with the achiral Zn-porphyrin functionalized with other and more effective chiral dyes, chiral semi-conductors, and chiral catalysts, but a proof-of-principle to make another counterintuitive approach is presented. The control of electrons’ spin in the chemical kinetics during the photochemical water splitting will also rejuvenate the field of magnetic field effects in chemical kinetics and related phenomenon as reviewed by Steiner and Ulrich many years ago, following the discovery and understanding of electron spin polarized phenomena during chemical reactions. 32 This is the more of importance due to the recent interest in photoredox catalysis in organic chemistry with exciting enantioselectivities. 33 In addition, the work points to the importance of chirality and spin selectivity in multiple electron reactions in biology.

**CONCLUSIONS**

The experimental results observed in the current study provide new insights into the mechanism behind oxygen formation in the oxygen evolution reaction and provide a new path for improving the efficiency of the water splitting process. Obviously, much work has to be done to optimize the system with other and more effective chiral dyes, chiral semiconductors, and chiral catalysts, but a proof-of-principle to make another counterintuitive approach is presented. The control of electrons’ spin in the chemical kinetics during the

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