Organic π-Conjugated Polymers as Photocathode Materials for Visible-Light-Enhanced Hydrogen and Hydrogen Peroxide Production from Water

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1. Introduction

Hydrogen is an important chemical feedstock and building block; it is used as a reductant in petroleum refining, ammonia synthesis, the manufacture of stainless steel, and the production of core chemicals (e.g., methanol) and food (e.g., margarine). The annual global market for hydrogen gas is 75 Mt in 2018, which is expected to increase continuously and rapidly.[1] Hydrogen is also regarded to be a critical and indispensable clean fuel for sustainable energy systems because of its extremely high energy density of 142 kJ g⁻¹ (vs 44 kJ g⁻¹ for gasoline) and low pollution emissions.[2] However, hydrogen is presently produced by conversion of hydrocarbons or fossil fuels and is accompanied by enormous energy consumption and greenhouse gas emissions.

Electrolytic water splitting for the production of hydrogen can be achieved using the excess electricity generated by photovoltaics.[3] Hydrogen can be used as fuel locally or reconverted into electrical energy with via fuel cells on demand. However, the energy lost during electrical conversion and chemical reaction is not small; hence, a more direct approach that uses the energy of sunlight to produce hydrogen in an on-site manner is strongly desired.

The production of hydrogen through photo(electro)catalytic water-splitting has been extensively investigated using inorganic semiconductors, including metal oxides, such as TiO₂, Cu₂O, and Ga₂O₃, and chalcogenides such as CdS and CdSe.[4] This research was triggered by TiO₂-catalyzed water-splitting that evolves oxygen when illuminated and is nowadays the benchmark photocatalyst for photoenergy conversion studies and the photo-oxidations of organic components during water and air purification.[5] While TiO₂ is characterized by a legendary long lifetime of holes to oxidize water,[6] TiO₂ absorbs only in the UV region due to its wide bandgap and is unable to reduce water to hydrogen and oxygen gases evolved from the inorganic semiconductors, which are often unstable in aqueous acidic and/or alkaline solutions, are frequently composed of precious or toxic metals, and the reaction often requires the assistance of a sacrificial reagent or a significant bias voltage. Separating the hydrogen and oxygen gases evolved from the inorganic semiconductor particles suspended in water is also problematic.

Photoelectrocatalytic water-splitting has also been studied using pure organic semiconductors as alternatives to

The photo(electro)chemical reduction of water and oxygen to produce hydrogen (water-splitting) and hydrogen peroxide, respectively, are well developed with inorganic semiconductors. In contrast, organic π-conjugated polymers, especially precisely synthesized ones, have been extensively studied as photoharvesting and charge-separating materials in dry photoelectron-conversion devices, such as organic photovoltaic cells. However, the use of conjugated polymers as photocathodes; i.e., photoelectrocatalytic reduction-active materials in direct contact with aqueous electrolytes, has been less explored.

This review describes the fundamentals of the electrochemistry of water and oxygen reduction, as well as organic semiconductor functions for photocathode activity in water, along with figures of merit for organic photocathodes used to practically produce hydrogen and hydrogen peroxide. Recent research on conjugated polymers in this field is then surveyed after briefly referring to early trial-and-error investigations using conventional conjugated polymers. Basic and very simple designs of robust polythiophene films are demonstrated as examples of successful materials which act as both visible-light harvesters and catalysts for hydrogen evolution and the production of hydrogen peroxide, and as counterparts in combination with conventional oxygen-evolution catalysts. Perspectives for this emerging field are also briefly provided.

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inorganic ones, as has been cited in the previous perspective\(^\text{[8]}\) and reviews.\(^\text{[9]}\) Among them, \(\pi\)-conjugated polymers have advantages over their inorganic counterparts, including tunable photoresponsiveness that is achieved through molecular design, high charge carrier mobility, and components that are potentially derived from renewable sources.\(^\text{[10]}\) Some \(\pi\)-conjugated polymers satisfy the following requirements for photo(electro)catalytic water-reduction capability:\(^\text{[11]}\) visible-light absorption with a high absorption coefficient, an appropriate lowest unoccupied molecular orbital (LUMO) that matches the energy of the hydrogen evolution reaction, and high charge carrier mobility in the material. The photocatalytic capabilities of \(\pi\)-conjugated polymers for water reduction have initially been examined by employing polymer particles in the presence of sacrificial donors or reducing agents, such as triethanolamine and ascorbic acid, that compensate for the water oxidation reaction at the counter electrode.\(^\text{[12]}\) While suspensions of polymer particles in aqueous solutions of sacrificial reagents display both visible-light harvesting and catalytic activity when irradiated, such combinations that use large excesses of sacrificial reagents are far from sustainable and practical for the production of hydrogen from water.

Another inherent advantage of a polymer is its facile film-forming processability. Research into photo(electro) catalytically responsive films or layers on current-collecting (transparent) substrates as photocathodes for water reduction has progressed; these materials were formed using conventional \(\pi\)-conjugated polymers as well as newly designed ones, or by blending polymers as bulk heterojunctions. While hydrogen-production rates obtained using these conjugated-polymer film-based photocathodes were lower than those of their inorganic and/or particle-based counterparts, some current organic cathodes have boosted rates that are comparable to those of inorganic semiconductors. A polymer-film-based photo(electro)catalytic cathode is illustrated (see the figure in the Table of Contents and Figure 3), in which cathode plates are immersed in a pool of water in sunlight for hydrogen evolution; these plates are simply connected by a conducting wire to a water-oxidation catalyst plate immersed in the branched counter pool for the separate evolution of oxygen.\(^\text{[13]}\) This challenging process is operated without any applied bias and proceeds via a one-photon-per-electron pathway to produce hydrogen.

Hydrogen peroxide (H\(_2\)O\(_2\)) is an active reagent in a number of oxidation reactions that produces only water and oxygen and no hazardous byproducts, and is widely and industrially used for pulp and paper bleaching, in textile processing, during the production of electronics, and for wastewater treatment.\(^\text{[14]}\) The formation and decomposition of H\(_2\)O\(_2\) are also important processes, as the active species formed are involved in a plethora of biological processes. For example, the oxidizing power of H\(_2\)O\(_2\) facilitates the decontamination of biological contaminants, including pandemic viruses.\(^\text{[15]}\) H\(_2\)O\(_2\) is also a promising alternative to hydrogen as a green energy carrier, since the energy density of 60 wt% aqueous H\(_2\)O\(_2\) (3.0 M) \(\text{L}^{-1}\) is comparable to that of hydrogen compressed at 35 MPa (2.8 M) \(\text{L}^{-1}\); hence H\(_2\)O\(_2\) can be used as a fuel to generate electricity.\(^\text{[16]}\) The annual global market for H\(_2\)O\(_2\) is currently 3 Mt, which is expected to double in the coming decade.\(^\text{[17]}\)

H\(_2\)O\(_2\) is theoretically formed from abundant water and oxygen; however, the majority of global H\(_2\)O\(_2\) is manufactured by the anthraquinone process,\(^\text{[14a]}\) which involves the hydrogenation of an alkylanthraquinone precursor dissolved in an organic solvent, with subsequent reduction of oxygen and liquid–liquid extraction to recover H\(_2\)O\(_2\). The major drawbacks of this multistep process include the requirement of massive infrastructure, significant energy input, and centralized production that requires additional transport, storage, and handling of highly concentrated H\(_2\)O\(_2\), which is unsafe and hazardous. Dilute H\(_2\)O\(_2\) solutions are sufficient for most applications, with less than 0.1% required for wastewater treatment and dilute alkaline H\(_2\)O\(_2\) used during paper bleaching.

Electrochemical oxygen reduction provides a comprehensive H\(_2\)O\(_2\)-production route suitable for the on-site generation of H\(_2\)O\(_2\) during pulp and paper bleaching, and water and wastewater treatment, respectively.\(^\text{[18]}\) Although electrochemical H\(_2\)O\(_2\) production has been further progressed using more efficient catalysts,\(^\text{[19]}\) such as AuPd and carbon nitrides, and by the engineering of electrochemical reactors, costs associated with electricity and electrolyzer maintenance are significant; hence, H\(_2\)O\(_2\) production in a more sustainable and on-site manner is an increasing requirement.

Much effort has been directed toward solar-driven photochemical H\(_2\)O\(_2\) production from oxygen and water as a simple and green process that has no additional energy demands. While inorganic semiconductors for the photochemical production of H\(_2\)O\(_2\) (e.g., ZnO) have a long history of research interest,\(^\text{[20]}\) they are insufficiently photocatalytic and often require the use of excess amounts of a sacrificial agent, such as formate or phenol; that is, H\(_2\)O\(_2\) is produced through a cascade of reductive reactions involving a sacrificial reducing agent, photoirradiated semiconductor particles, and oxygen in water. Photocatalysts that do not require any additive have been sought after by focusing on graphitic carbon nitrides\(^\text{[21]}\) and their oxygen-enriched derivatives,\(^\text{[22]}\) and by developing visible-light-absorbing heterojunctions from melamine and WO\(_3\), and by covalently combining the polyoxometalate \([\text{PW}_{11}\text{O}_{39}]^{7–}\) cluster with a microporous graphitic carbon nitride.\(^\text{[24]}\) However, despite this significant research effort, the performance of visible-light-driven photochemical H\(_2\)O\(_2\)-production methods remains insufficient due to low rates. Photoelectrocatalysts or photocathodes for the reduction of oxygen to H\(_2\)O\(_2\) have also been investigated with the aim of achieving higher catalytic rates in the presence of an additional bias potential, where the photocathode involves an organic dye.\(^\text{[23]}\) Although H\(_2\)O\(_2\)-production rates exceeded those of previously reported photocatalysts, the electrochemical cells required significant bias voltages (0.6–1.0 V) and were operated at pH \(\leq 7\) because the catalysts are unstable under alkaline conditions. A practical cell configuration for reductive H\(_2\)O\(_2\) production must include a counter electrode for catalytic oxygen evolution from water. As traditional water-oxidation catalysts, such as MnO\(_2\) and RuO\(_2\), function optimally at high pH,\(^\text{[24]}\) a photocatalytic cathode that can function at high pH and yield a photovoltage that exceeding the voltage between the reduction of oxygen to H\(_2\)O\(_2\) and the oxidation of water is ideal. \(\pi\)-Conjugated polymers have recently been studied as photocathode materials that possibly fulfill these criteria for H\(_2\)O\(_2\) production. A prototype polymer-film-based electrode plate for H\(_2\)O\(_2\) production is illustrated in Figure 17a.\(^\text{[25]}\)

As introduced above, the photo(electro)chemical reductions of water (or water-splitting) and oxygen, which evolve hydrogen and produce hydrogen peroxide, respectively, have been and
continue to be developed through extensive researching and by finely tuning inorganic semiconducting materials. On the other hand, typical organic semiconductors, namely \( \pi \)-conjugated polymers, such as polythiophenes and poly(phenylenevinylene) s, including their precisely synthesized derivatives, have been extensively studied as photoharvesting, photoemitting, and charge-separating materials, and have been successfully used in photoelectronic devices, including organic photovoltaic cells. However, these examples involve solvent-free and dry devices, with the latest new frontier involving the application of such conjugated polymer films as photocathodes (i.e., photovoltaic catalytic reduction-active materials in direct contact with aqueous electrolytes). This article focuses on organic semiconducting \( \pi \)-conjugated polymers as photocathode films or coating materials that catalytically act to reduce water, evolve hydrogen, and reduce dissolved oxygen to produce \( \text{H}_2\text{O}_2 \), i.e., on the limited overlapping scope of three domains of \( \pi \)-conjugated polymer films, visible-light-driven electron-injection reactions, and reductive reactions of water and oxygen.

The first part of this article discusses the fundamentals of electrochemical water-splitting and the reduction of water and oxygen, by considering the electrochemical kinetic and equilibrium of the reductive reactions, and the organic-semiconducting function required for photocathode activity in contact with water. The figures of merit for an organic photocathode to practically produce hydrogen and \( \text{H}_2\text{O}_2 \) are then noted. In the second part, we survey and summarize recent research into \( \pi \)-conjugated polymer materials in this area after briefly discussing early trial-and-error attempts using conventional conjugated polymers. We finally demonstrate the first, basic, and very simple designs of single-component polythiophene films as examples of successful robust materials that act as both visible-light harvesters and catalysts for hydrogen evolution and \( \text{H}_2\text{O}_2 \) formation in combination with conventional oxygen-evolution catalysts. A short perspective of this emerging area is also provided.

Research into visible-light-conversion devices and systems that practically produce hydrogen (and \( \text{H}_2\text{O}_2 \)) fabricated with photocathodes that partially include \( \pi \)-conjugated polymer films has been well summarized in the recent reviews. A comprehensive review of the devices and the photoelectrodes based on organic semiconductors have also recently been published.

2. Fundamental Properties and Photoelectrochemical Characterization of the Water and Oxygen Reductions As Well As Organic Photocathode Materials

Electrochemical water-splitting has been intensively studied for two centuries, including its basic chemistry and its large-scale engineering. The overall water-splitting reaction is described by the following equilibrium equation

\[
2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2
\]

The Gibbs free energy change \( \Delta G^0 \) for water-splitting to give hydrogen and oxygen under standard conditions (the activities of all species = 1, ambient pressure = 1 atm, temperature = 298.15 K) is 237.2 kJ \( \text{mol}_{\text{H}_2\text{O}}^{-1} \). This value is extremely large in comparison with, for example, the decomposition of ammonia (2 \( \text{NH}_3 \) \rightleftharpoons \( \text{N}_2 + 3 \text{H}_2 \)), which has a \( \Delta G^0 \) of +16.5 kJ \( \text{mol}_{\text{NH}_3}^{-1} \), highlighting the fundamental difficulty associated with the water-splitting reaction, which is due to the extremely large enthalpy change (\( \Delta H^\circ = 286 \text{ kJ mol}_{\text{H}_2\text{O}}^{-1} \)) that results in a strongly endothermic reaction. For example, heating water steam to 2200 °C gives an equilibrium with the formation of \( \approx 3\% \) hydrogen.

The free energy change \( \Delta G^0 \) associated the water-splitting reaction, Equation (1), can be converted into the standard potential \( E^0 \) for the overall equilibrium reaction (the theoretical cell voltage for the electrolytic reaction) using the following relationship [Equation (2)]

\[
\Delta G^0 = -nFE^0
\]

in which \( n \) and \( F \) are the number of electrons (here \( n = 2 \)) and Faraday’s constant (9.649 \( \times 10^4 \) C mol\(^{-1} \)), respectively. \( E^0 \), or the thermodynamically required voltage to split the water molecule into hydrogen and oxygen in the water electrolysis cell, is calculated by Equation (2) to be 1.229 V.

The following sections briefly presents the electrochemical fundamentals of the cathodic reactions reported in this review, i.e., the reductions of water and oxygen and the associated photocatalytic reactions.

2.1. Water Reduction

Water splitting is described by two half-reactions: the hydrogen evolution reaction as the electron-accepting reductive reaction of water or a proton [Equation (3)], and the oxygen-evolution reaction as the electron-releasing oxidative reaction of the water molecule [Equation (4)] (more exactly, protons exists in water as hydronium ions, \( \text{H}_3\text{O}^+ \)).

\[
2\text{H}^+ (aq) + 2e^- \rightleftharpoons \text{H}_2 (g)
\]

\[
\text{O}_2 (g) + 4\text{H}^+ (aq) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(l)
\]

where \( E^0 = 0.000 \text{ V} \) versus the standard hydrogen electrode (SHE), which is calculated from \( \Delta G^0 \) to be 0.000 kJ mol\(^{-1} \).

The hydrogen evolution reaction conventionally proceeds with high efficiency under highly acidic conditions, as represented by the proton-reduction reaction [Equation (3)]. Here the reductive reaction of an oxidized species (\( \text{O}_x \)) to form a reduced species (\( \text{Red} \)) (\( \text{O}_x + ne^- \rightleftharpoons \text{Red} \)) is in electrochemical equilibrium and obeys the Nernst equation [Equation (5)]

\[
E = E^0 + \frac{RT}{nF} \ln \left( \frac{a_{\text{Red}}}{a_{\text{O}_x}} \right)
\]

in which \( E \) is the equilibrium potential, and \( R, T, \) and \( a_i \) are the universal gas constant, the temperature, and the activity of species \( i \). By applying the Nernst equation to the
two-electron reductive reaction of two protons that evolves molecular hydrogen [Equation (3)], \( E \) can be calculated under nonstandard conditions (\( R = 8.314 \) J K\(^{-1}\) mol\(^{-1}\) (converted to \( 8.314 \times 10^{-3} \) atm L K\(^{-1}\) mol\(^{-1}\))) on the SHE scale (\( E^\circ = 0 \) V) as follows:

\[
E = E^\circ + \frac{R T}{2 F} \ln \left( \frac{[\text{H}^+]^2}{[\text{H}_2]} \right)
\]

Under 1 atm of hydrogen, \([\text{H}_2] = 1\), so:

\[
E = \frac{R T}{2 F} \ln([\text{H}^+]^2) = \frac{R T}{F} \times \ln([\text{H}^+])
\]

-\(\ln([\text{H}^+])\) is then converted to \(-\log([\text{H}^+])\) or \(pH\), where \( \log e = 0.4343 \), to give:

\[
E = \frac{R T}{F} \times \left( \frac{\log([\text{H}^+])}{\log e} \right) = \frac{R T}{F} \times \frac{1}{(-\log e)} \times \text{pH}
\]

Substituting the values of the constants and standard temperature (298.15 K) into the above equation leads to Equation (6), where \( E \) versus SHE is referred to as the equilibrium potential (for the hydrogen evolution reaction) on the “reversible hydrogen electrode (RHE)” scale.

\[
E = -0.059 \times \text{pH} \ \text{V vs SHE} \quad (6)
\]

The hydrogen evolution reaction also proceeds under alkaline (high pH) conditions, and is represented by the two-electron-reduction reaction of two water molecules to form molecular hydrogen with the release of hydroxide anions:

\[
2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^- (aq) \quad (7)
\]

where \( E^\circ = -0.828 \) V versus SHE, as calculated using \( \Delta G^\circ = +159.8 \) kJ mol\(^{-1}\).[21] The Nernst equation for this reaction gives \( E \), as follows:

\[
E = -0.828 + \frac{R T}{2 F} \ln \left( \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2][\text{OH}^-]^2} \right) \quad (8)
\]

The ionization constant for water \( K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \) (at 298.15 K); hence, \([\text{OH}^-] = K_w/[\text{H}_2\text{O}]\) is introduced to replace \([\text{OH}^-]\) with \([\text{H}^+]:\)

\[
E = -0.828 + \frac{R T}{2 F} \ln \left( \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2][K_w][\text{H}^+]^2} \right) = -0.828 + \frac{R T}{2 F} \ln \left( \frac{[\text{H}^+]^2}{[\text{H}_2][K_w]} \right)
\]

Under 1 atm of hydrogen, \([\text{H}_2] = 1\), and the conversion of \(\ln([\text{H}^+])\) into \(pH\) gives:

\[
E = -0.828 + \frac{R T}{2 F} \times 2 \times \ln \left( \frac{[\text{H}^+]}{K_w} \right) = -0.828 + \frac{R T}{F} \times \frac{1}{(-\log e)} \times (-\log([\text{H}^+]^{2} + \log(K_w)))
\]

After substituting in the values of the constants, the \( E \) for the reaction in Equation (8) is also given by Equation (6).

The use of the same equation (Equation (6)) indicates the reversible potential \( E \) noted versus RHE for the hydrogen evolution reaction under acidic and alkaline conditions, as depicted in Equations (3) and (7), respectively. Importantly, although the equilibrium potential of the hydrogen evolution reaction shifts with \( pH \) on the SHE scale, equilibrium potentials normalized against \( pH \) (noted vs RHE) using Equation (6) can effectively be used to compare the experimental results for water with different \( pH \) values under the assumption that a Nernstian equilibrium exists. The experimental relationship between \( pH \) and reaction performance needs to be checked with great care; for example, the \( pH \)-independent performance on the \( E \) versus SHE scale or the \( pH \)-dependent one on the \( E \) versus SHE scale.

For the counterparts to the hydrogen evolution and water-reduction reactions, namely the oxidative reactions of water that evolve oxygen, are represented by the oxidation of molecular water (Equation (4)) and by the oxidation of the hydroxide anion (produced in Equation (7)) at high \( pH \) (Equation (9)). The \( E^\circ \) value for Equation (9) has been determined with the \( \Delta G^\circ \) value for Equation (4)[13]

\[
\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightleftharpoons 4\text{OH}^- (aq) \quad E^\circ = +0.401 \ \text{V vs SHE} \quad (9)
\]

Based on the Nernst equation, the standard potential for water oxidation at various \( pH \) values is given by Equation (10), which is calculated in a similar way to Equation (6)

\[
E = (+1.229 - 0.059 \times \text{pH}) \ \text{V vs SHE} \quad (10)
\]

It is therefore essential that the potential difference between the hydrogen- and oxygen-evolution reactions through water-splitting (or the theoretical (minimum) cell voltage for water-splitting) is 1.229 V under all \( pH \) conditions (Figure 1a).

### 2.2. Oxygen Reduction

Hydrogen peroxide can theoretically be generated from water and oxygen through Equation (11), with a \( \Delta G^\circ \) of \(-16.8 \) kJ mol\(^{-1}\), and gives \( E^\circ = 1.210 \) V versus SHE[31] using Equation (2)

\[
\text{H}_2\text{O}(l) + 1/2 \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}_2(l) \quad (11)
\]

One of the half-reactions is the two-electron reduction of dissolved oxygen in water to produce \( \text{H}_2\text{O}_2\), as shown in Equation (12)[10]

\[
\text{O}_2(g) + 2\text{H}^+ (aq) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}_2(l) \quad E^\circ = 0.695 \ \text{V vs SHE} \quad (12)
\]

In the counter half-reaction, the two-electron oxidation of water proceeds as follows[9]

\[
\text{H}_2\text{O}_2(l) + 2\text{H}^+ (aq) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E^\circ = 1.763 \ \text{V vs SHE} \quad (13)
\]

Oxygen reduction proceeds at a more favorable potential than water reduction (Figures 1 and 2). In other words, water reduction takes place after careful removal of dissolved oxygen.
Another route for the production of hydrogen peroxide is shown in Equation (14), with the corresponding half-reactions shown in Equations (12) and (4)

\[ \text{O}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}_2(l) + \frac{1}{2}\text{O}_2(g) \quad E^\circ = 0.605 \text{ V vs SHE} \quad (14) \]

\[ \frac{1}{2}\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \rightleftharpoons \text{H}_2\text{O}(l) \quad E^\circ = 1.229 \text{ V vs SHE} \quad (4) \]

At higher pH than the pK_a of H_2O_2 (11.6), oxygen reduction follows Equation (15) to form HO_2^−, with E^\circ = 0.74 V versus RHE at pH 13\(^{[32]}\)

\[ \text{O}_2(g) + \text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{HO}_2(aq) + \text{OH}^- (aq) \quad E^\circ = +0.358 \text{ V vs SHE} \quad (15) \]

HO_2^− is regarded as a H_2O_2 equivalent and instantaneously reacts with a proton to form H_2O_2. Application of the Nernst equation to these oxygen-reduction reactions (< pH 11.6) gives a pH dependency of −59.1 mV pH\(^{-1}\), very similar to values for water-reduction reactions (Figure 1b).

The two-electron reduction of water to H_2O_2 occurs through a single-electron reduction to form the superoxide radical anion O_2^−, a single-electron reduction with a proton to HOO^−, a four-electron reduction to H_2O, and complicated self-decomposition reactions.\(^{[33]}\)

Figure 2 shows the standard potentials for water and oxygen reduction, water oxidation, and related reactions, with typical reversible redox reactions as controls.

### 2.3. Organic Semiconductors as Photocathode Materials

Some semiconductors efficiently absorb light and catalyze the redox reactions of water or the production of hydrogen and oxygen from water, which directly serve photocatalytic and photoelectrocatalytic water-splitting. The light irradiation of an organic semiconducting material generates an exciton or an electron–hole pair that may be separated into an electron and a hole. When immersed in water, the electron can be injected to a proton or to water to produce hydrogen. In the counter process, the separated hole diffuses in the other direction under a bias potential for photoelectrocatalytic oxygen production or the equilibrium potential of the water-oxidation on the anode, and is transferred to a hole-conducting substrate connected to an electrically conducting wire (Figure 3).

Photo(electro)catalytic water splitting historically began with the discovery that the TiO_2 inorganic semiconductor evolves oxygen when very simply irradiated with UV light\(^{[5]}\) (the potential required to oxidize water with TiO_2 is shown at the most-left side of Figure 4). Inorganic semiconducting materials capable of splitting water when irradiated with visible light have been, and continue to be, extensively researched. Semiconductors with adequate bandgap energies (E_g) to absorb light from the solar spectrum (absorption edge = 1240/E_g, e.g., 2 eV → light
absorption at <620 nm) have electrons from their valence bands (blue in Figure 4) excited to their conduction bands (red), which leads to the formation of electrons and holes in the conduction and valence band, respectively. Band energy levels need to be adequately positioned with respect to the water redox pair, i.e., the conduction band edge must be shallower than the water-reduction potential, while the valence band edge must be at a deeper potential than the water-oxidation potential. The photogenerated electron and hole need a sufficient driving force to advance the reduction and oxidation processes, respectively. However, few inorganic semiconductors possess appropriate bandgaps to absorb visible light, and very few have band edges suitable for water oxidation and reduction (e.g., CdS in Figure 4). Hence, they have often been examined in reactions assisted by sacrificial reagents, of a catalyst combination, and/or the application of an external bias voltage.

Another method involves coupling two semiconductors (e.g., ZnO and Cu2O; Figure 4), which is referred to as the Z scheme process and was inspired by photosystems I and II in natural photosynthesis. The photogenerated electron in the conduction band of one of the semiconductors is transferred to the valence band of the other or, alternatively, both semiconductors are connected in series. Such a process is not easily facilitated due to reverse charge-transfer or charge-recombination processes, and the principle of two photons per electron process limits its efficiency.

As alternatives to inorganic semiconductors, organic semiconducting materials or π-conjugated polymeric materials have optimized bandgap values that balance both visible-light energy use and photovoltage development; examples of such polymers are shown in the right half of Figure 4. The energies of the LUMO and the highest occupied molecular orbital (HOMO) of a polymer (which correspond to the conduction and valence band edges of an inorganic semiconductor) need to be appropriately aligned at between −3.0 and −3.5 eV and −5.0 and −6.0 eV, respectively, for water reduction and oxidation in an aqueous electrolyte, respectively, in order to establish the thermodynamic driving force for photoreduction or photooxidation. A narrow HOMO–LUMO that corresponds to a bandgap of 1.5–2.5 eV is also required for visible-light absorption. Some π-conjugated polymers harvest visible light with very

Figure 3. Cell configuration of the semiconductor photocathode and a counter anode with applied bias potential, and proton and oxygen reduction and water oxidation reactions with the scale of redox potential and energy level. e−: electron, h+: hole, CB: conduction band, and VB: valence band.

Figure 4. Typical inorganic and organic semiconductors (the left and right, respectively) with their valence/conduction bands and HOMO/LUMO levels, respectively. Potentials for the water-reduction and -oxidation are indicated with dashed lines (adjusted to pH at which the corresponding material was measured). PPV: Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene].
high absorption coefficients (>10^4 cm^−1). In addition, favorable exciton and charge mobility is required in the polymer thin film in order to reduce charge recombination during exciton generation and transport. Hole mobilities are relatively high, at 10−1 to 10−3 cm^2 V−1 s−1,[10] for the typical π-conjugated polymers discussed in this article.

The photo(electro)catalytic process in an organic conjugated polymer can be viewed as a four-step process (Figure 5), as follows:

1) Light absorption: A photon with energy greater than or equal to the HOMO–LUMO gap (or bandgap) of the polymer is absorbed by the polymer (a thickness of 50–200 nm is required for efficient absorbance). The excitation of an electron from the HOMO of the polymer to its LUMO generates a coulombically bound electron–hole pair or an exciton. The exciton is usually in an excited or transition singlet state S_1↑↓ formed from the ground singlet state S_0↑↓. Some transfer to the excited triplet state T_1↑↑ occurs via intersystem crossing; the former radiatively emits fluorescence with a wavelength that almost corresponds to the HOMO–LUMO gap, while the latter phosphoresces at a longer wavelength.

2) Exciton diffusion: The exciton diffuses in the polymer film within its restricted length; the effective diffusion lengths for singlet and triplet excitons have been determined to be ~10 and 100 nm, respectively,[35] with the latter more efficient for charge separation in subsequent reactions.

3) Charge transfer at the polymer–electrolyte-solution interface: Some photoexcited excitons reach the interface and separate into their constituent charges—a, i.e., the electrochemical reaction takes the role of a junction: The electron is injected into water (to reduce a proton, a water, or an oxygen molecule), while the hole remains in the polymer domain. Excitons are generated homogeneously in the polymer layer, so only the ones created within their effective diffusion lengths can contribute to the photoconversion. Outside of the diffusion length, the excitons disappear via recombination of the excited electron and hole.

4) Hole-migration: The majority of organic polymers are p-type or hole-transporting semiconductors; therefore, holes remaining in the polymer migrate toward the polymer–substrate interface (left in Figure 5), are extracted at the substrate and supplied for use in the counter reaction through an external circuit. Holes are consumed through chemical redox reactions with the reagent instead of being extracted at the substrate in systems that use a sacrificial reagent without substrates.

In step 3), an oxidized species, such as a proton in solution, accepts the exited electron from the conduction band (or LUMO) of the polymer when the band level is more negative (shallower) than the reduction potential of the oxidized species during contact between the photoexcited semiconducting polymer layer and the electrolyte solution. At the interfacial edge of the conduction band, the Fermi level faces the reduction potential of the oxidized species; hence, the electron transfers smoothly with band bending (as illustrated in Figure 6). In step 4), the remaining hole migrates along the bent valence band (or HOMO) edge toward the bulk polymer.

2.4. Electrochemical Kinetics at the Cathode for Water Reduction

Even if the potential of the electrode or electrocatalyst is sufficiently enhanced to exceed thermodynamic requirements, the redox reaction of a reactant in the electrolyte solution does not always proceed. Appreciable electrical currents or electrode reaction rates are attainable only when the kinetic overpotential (or activation energy) is overcome.

The reaction rate of the catalytically active electrode is represented by the current density J (A cm−2)

\[ J \propto k_{\text{red}}c_{\text{ox}} - k_{\text{ox}}c_{\text{red}} \]  \hspace{0.5cm} (16)

Which is proportional to the difference in the reduction and oxidation rates (k and c are the reduction and oxidation rate constants and concentrations of oxidized and reduced species, respectively). J is apparently zero when the potential applied to the electrode reaction is equal to the redox potential of the ox/red pair. The kinetic current density at this equilibrium point is
referred to as the “exchange current density” ($i_0$); it reflects the activation energy of the electron-transfer reaction at the electrode–solution interface and depends on the electrode-active material.

The relationship between the (kinetic) current density ($i$) at an applied potential and $i_0$ can be analyzed using the Tafel Equation (17)

$$\log i = \log i_0 + \alpha \eta / 0.059 \quad (17)$$

where $\alpha$ is the asymmetric parameter of the activated state of the electrode reaction, 0.059 is calculated from $\ln(\alpha) (RT/F)$, and $\eta$ (V) is the deviation of the applied potential from the equilibrium potential, and corresponds to the overpotential required for the reaction to proceed. $\eta$ reflects the excess electrical energy required to progress the electrode reaction. As an example of water electrolysis, the Tafel equation reveals that a kinetically less active electrode material with an $i_0$ of nA cm$^{-2}$ has $2 \eta$ of ~0.6 V for water electrolysis to progress. The exchange current density $i_0$ dominates the electrode reaction overpotential, and is inherent to the combination of redox reactions associated with the species in the electrode material.

The interface exhibits a capacitive component when a potential is applied to the electrode. The entire array of charged species at the electrode–solution interface is referred to as the “electrical double layer.” For example, excess electrons on a cathode with a negative potential are balanced by excess positive species at the electrode surface, and the formed product desorbs and diffuses back into the bulk phase. The real electrode reaction involves many processes within the electrical double layer or on the electrode surface, such as reactant adsorption, electron transfer, reactant bond cleavage, rearrangement, product formation on the electrode surface, and desorption of the product. All of these steps and their activation energies determine the overpotential and reaction efficiency of the electrode reaction.

The mechanisms associated with adsorption and subsequent chemical reactions during water and oxygen reduction have been extensively studied for metal and inorganic electrodes; however, few organic-based electrodes have been studied.

### 2.5. Counter Electrode Reactions

Photoexcited electrons are used to reduce protons, water, or oxygen molecules in the aqueous electrolyte to evolve hydrogen gas or to produce $\text{H}_2\text{O}_2$ at the photcathode, as the working electrode. These cathodic reductive reactions are balanced in three ways: 1) by applying an external voltage (a half cell), 2) by compensating through the oxidation of a sacrificial reagent, and 3) by oxidizing water to evolve oxygen gas. The first way is direct, quantitatively clear, and used in subsequent sections of this review when presenting and evaluating the activities of polymer-based photocathodes. Needless to say, this method is not sustainable, the consumption of electrical energy is not cost effective, and the applied electrical bias needs to be as small as possible, or zero, by modifying the cell configuration and working conditions.

Sacrificial reagents and reductants have been researched for use in the counter oxidation reaction during studies into photocatalytic hydrogen production. The coexistence of excess sacrificial reagent is crucial for research that uses photocatalytic powder, including conjugated polymers. Examples include methanol, ethanol, glycerol, glucose, ascorbic acid, triethyamine, triethanolamine, and ethylenediaminetetraacetic acid. For example, methanol is irreversibly oxidized through radical chain reactions to form formaldehyde, formic acid, carbon dioxide, and/or hydrogen gas. The oxidation potentials of ascorbic acid, triethyamine, and triethanolamine are 0.70, 0.93, and 0.95 V versus SHE, respectively$^{[36]}$ and they are strong unidirectional reducing reagents. The addition of excess sacrificial reagent is a simple and convenient way of studying the photocatalytic activities of water-reduction materials, but is practically inappropriate for use in water-splitting processes.

In the third way, the photocathode is connected by a wire to the counter-catalyst electrode where water is oxidized to oxygen gas in accordance with Equations (4) and (9) in the dark. As a result of water oxidation, the electrons withdrawn at the counter electrode travel through the external circuit and recombine with the holes at the working photocathode.

Many water-oxidation catalysts$^{[28]}$ have been researched and established based on their conventional use in anodes, for
2.6. Organic Photocathode Activity Parameters for the Reduction of Water and Oxygen

Photocathode voltammograms acquired using a standard three-electrode setup in aqueous acidic, neutral, or alkaline solutions provide the main figures of the merit (i.e., points (1)–(6) below) of their photoelectrochemical water and oxygen reduction capabilities (Figure 7).

1) The “cathodic or reduction photocurrent density” (in units of μ−mA cm−2 relative to the photocathode surface area), preferably at 0 V versus RHE (Figure 8). The ratio of the current density when illuminated (1 sun or simulated sunlight irradiation) to that in the dark, often under chopped illumination conditions, is usually given as the control. The current time-course is also informative, as it provides support for the reaction steady state and the durability of the photocathode. A current density of 1 mA cm−2 at 0 V versus RHE, which corresponds to almost 1% solar-to-hydrogen conversion efficiency, is often set as the benchmark for research. Current density at specific applied potential (denoted as mA cm−2 @ the potential V vs RHE) is also indicative of activity.

2) The “onset potential” is defined as the potential versus RHE at which the photocurrent density reaches a threshold, usually 10 μA cm−2 (see example in Figure 8). A slow voltammogram scan rate of 1 mV s−1 minimizes electrical-double-layer and diffusional effects. The given onset potential reflects the overpotential of the electrolytic reaction. A more positive onset potential widens the operating potential window for the reduction of water. The maximum power potential, another activity parameter, is the potential that saturates current density and is the maximum current density.

3) The “open-circuit potential” versus RHE under illumination. This potential indicates the “photovoltage” of the cathode; if it exceeds the theoretical potential for the oxidation of water (1.229 V), then unaided water electrolysis under illumination is thermodynamically possible.

4) The “gravimetric rate of hydrogen production” (molH2 h−1 gcat−1) is determined by normalizing the amount of hydrogen evolved through water reduction per hour and photocatalyst (or the photocathode-active material) weight, and its benchmark for research is 1 molH2 h−1 gcat−1. For oxygen reduction, the amount of produced hydrogen peroxide is determined by redox titration or spectrophotometry. The benchmark value for research is 1 molH2O2 h−1 gcat−1, often for 50 mL of water in oxygen at 1 atm.

5) “Faradaic efficiency” is the molar percentage of product per passed current in an electrolysis reaction. The faradaic efficiency for water reduction is calculated by dividing the amount of evolved hydrogen, as monitored by gas chromatography, by the theoretical amount of hydrogen determined from the reduction current. Faradaic efficiencies should be greater than 90% when experiments are performed under reasonable electrochemical conditions (applied potentials and electrolyte compositions). For the production of hydrogen peroxide, faradaic efficiencies should also exceed 90%, but they are affected by the conditions used, which can facilitate side-reactions leading to decomposition. In any case, faradaic efficiency is not applied to electrical-bias-free systems.

6) “Turnover number” is the number of moles of produced hydrogen or hydrogen peroxide per molar number of catalytic active sites (for example, the calculated active photocathode-material units). “Durability” is assessed for the long-term by recording photocurrent density or the production rate when continuously illuminated.
“Photoresponse action spectra,” which are the comparison of UV–visible absorption spectra of the photocathode material versus reduction current densities at a particular wavelength, and are also indispensable when discussing the contribution of the photocathode material to photoelectric performance. Band-path and interference filters are used to obtain monochromatic light during the acquisition of action spectra. The wavelength dependency of current density does not always respond to the absorption spectrum, even when the photocathode material absorbs visible light.

Apart from three-electrode systems, the correct measurement of incident light power or photons provides the following parameters that highlight the capability of the photocathode. While photodiodes are used to measure the number of incident photons, errors associated with surface scattering are involved, and an apparent number is provided.

“Apparent quantum yield,” which is given by

\[
\text{Quantum yield} = \frac{\text{Number of reacted electrons}}{\text{(2 electrons} \times \text{produced hydrogen or H}_2\text{O}_2 \text{molecules})/ (\text{the number of incident photons})}
\]

“Incident photon-to-current efficiency (IPCE)” is the apparent quantum yield at each wavelength. Previously reported IPCE values for organic photocathodes are below a few percent.

“Solar-to-hydrogen conversion efficiency”: The conversion efficiency under 1.0 sun irradiation is defined as

\[
\text{Conversion efficiency} = \frac{\text{Evolved hydrogen output energy}}{\text{(incident solar energy)} = \frac{\text{[(mmol}_{\text{H}_2}s^{-1}) \times \text{237 kJ mol}^{-1}]}{\text{[(incident light power density} \times \text{(W cm}^{-2}\times \text{area} \text{(cm}^2\text{)})]]}
\]

If the amount of evolved hydrogen cannot be measured directly, then the conversion efficiency is calculated from electrochemical parameters to give the “solar conversion efficiency”

\[
\text{Solar conversion efficiency} = \frac{\text{[photocurrent density] \times (1.23 – \text{[bias potential]} \times \text{[faradaic efficiency]}}}{\text{(power density of the incident light)}}
\]

Photocurrent densities and the rates of hydrogen evolution and H\text{2O}_2 formation are strongly dependent on the experimental procedures and conditions. Photocathode performance is discussed by carefully comparing these activity parameters.

3. Light-Enhanced Hydrogen Production with \(\pi\)-Conjugated Polymers: Early Trials Using Conventional Polymers and High-Performing Designed Polymers

The simplest \(\pi\)-conjugated polymer is polyacetylene (I); after Shirakawa first synthesized high quality polyacetylene films, his group extensively characterized these novel films, including their photoelectrochemical properties (as illustrated in Figure 9a). Their 1981 paper stated to aim at an organic electrode material for photovoltaic energy conversion. A \(\approx\)5 \(\mu\)m thick self-standing film of I was connected to a lead wire using silver paste and set up as the working electrode in deoxygenated aqueous acetate buffer, with Pt and Ag/AgCl as the counter and reference electrodes, respectively. A reduction photocurrent of \(\approx\)5 \(\mu\)A cm\textsuperscript{-2} with the evolution of hydrogen gas was observed at \(-0.46\) V versus RHE and pH 5.7 when irradiated at 700 nm. Several studies using other conjugated polymers were reported around the middle of the 1980s (Figure 10). For example, the photoelectrochemical responses of polythiophene (2), polypyrrole (3), and polyaniline films were reported which were prepared by the electrochemical polymerization of thiophene, pyrrole, and aniline, respectively, on indium tin oxide (ITO) glass plates, and undoped by the application of a negative potential. Films that were \(\approx\)100 nm thick were immersed in aqueous electrolytes; irradiation with a Xe lamp induced a reductive photocurrent with a density of 15–25 \(\mu\)A cm\textsuperscript{-2} levels. These early reported conjugated polymer films were prepared in situ and were often intractable and lack of sufficient characterization.

In 1985, Yanagida et al. reported for the first time, photocatalytic hydrogen evolution from a suspension of poly(\(p\)-phenylene) (4) in water in the presence of a large excess...
of a sacrificial reagent when irradiated at above 290 nm. The reduction of water and hydrogen evolution were carefully checked using D$_2$O. Polymer 4 was in the form of a pale-yellow porous powder that exhibited a bandgap of 2.9 eV and was prepared by the polycondensation of 1,4-dibromobenzene using a magnesium Grignard reagent. A hydrogen evolution rate of 7 µmol h$^{-1}$ g$_{\text{polymer}}$ was observed in sacrificial diethylamine/water (2/1 v/v), but was less than 3 µmol h$^{-1}$ g$^{-1}$ when irradiated with visible light (>400 nm). Early research into light-driven hydrogen evolution using π-conjugated polymers, both as films with electrical bias and as powders in the presence of sacrificial reagents was thus occurring, but the interest then faded away for two decades.

A noteworthy exception is the poly(3-hexylthiophene) (5) film-based photocathode reported in 1996 by Holdcroft et al.$^{[42]}$ A reductive photocurrent was observed when a 0.8 µm thick film with a 2.0 eV bandgap was irradiated with monochromatic 435 nm light in aqueous solutions containing 5 vol% acetonitrile (to swell the film surface) at pH 2–12. A current density of 2.5 µA cm$^{-2}$ at pH 2.5 and −0.72 V versus RHE was reported. The photocurrent increased and the photovoltage linearly decreased with decreasing solution pH, which was ascribed to a proton reduction. Polymer 5 was in this case prepared by the polymerization of 3-hexylthiophene with excess FeCl$_3$ as the oxidizing reagent (it was difficult to exclude misgivings associated with Fe contamination). Almost two decades later (in 2013), the same group$^{[43]}$ was difficult to exclude misgivings associated with Fe contamination. They also introduced in the recent paper$^{[50]}$ oligoethylene glycol side-chains in the fluorene unit of the dibenzothiophene sulfone (R of $^{[48]}$) to give the polymer water-swelling property. The polymer powder exhibited the activity of 7.6 mmol g$^{-1}$ h$^{-1}$, which is almost 10-times higher than that of the previous 5-based film when 1-sun irradiated. The 5-based film fluoresced substantially less in aqueous acidic solutions, suggesting that photogenerated excitons are quenched by the protonation of the π-conjugated thiophene residue. The catalytic mechanism was proposed to involve protonation or self-acid doping at the surface of polythiophene 5, with subsequent hydrogen evolution and hole-transport in the bulk layer. However, the same group noted in their paper$^{[44]}$ in 2015 that no hydrogen gas was detected at the irradiated pristine 5-film, and that the photocurrent was largely due to residual oxygen in the solution.

In 2016, Cooper et al.$^{[45]}$ used donor–acceptor-type π-conjugated polymers to provide a bandgap of 2.7 eV. Suspended powder of typical polymer 7 in an aqueous solution of sacrificial methanol and tetraethylamine gave 1.5 mmol h$^{-1}$ g$^{-1}$ of hydrogen (200 times more than that of 4) when irradiated with a 300-W Xe lamp at above 420 nm; an apparent quantum yield of 2.3% was also noted. Triggered by the encouraging activity delivered by the narrow bandgap strategy,$^{[46]}$ conjugated fluorene and pyrene polymers 8, connected through ethynylene units, were synthesized by Chen et al. using cuprous-catalyzed coupling reactions,$^{[47]}$ which yielded significantly narrow bandgaps of between 1.64 and 1.89 eV, with activities of 4–6 mmol h$^{-1}$ g$^{-1}$ for their suspensions in sacrificial aqueous triethanolamine when irradiated at above 420 nm. Polymeric derivative of the dibenzothiophene sulfone$^{[48]}$ with the bandgap of the 2.1 eV exhibited the activity of 7.5 mmol h$^{-1}$ g$^{-1}$. Recently, Cooper et al.$^{[49]}$ analyzed the oligomers of dibenzothiophene sulfone with fluorene (7'), to elucidate high activity of the trimer ascribed to long-lived electrons generated under illumination. They also introduced in the recent paper$^{[50]}$ oligoethylene glycol side-chains in the fluorene unit of the dibenzothiophene sulfone copolymer (R of 7') to give the polymer water-swelling property. The polymer powder exhibited the activity of 2.9 mmol g$^{-1}$ h$^{-1}$ in the water/methanol/triethylamine (1/1/1) solution when irradiated with a Xe lamp, which was estimated to be 10% of apparent quantum efficiency at 420 nm. When cast as a thin film, the activity was further enhanced up to 13.9 mmol g$^{-1}$ h$^{-1}$. Cooper et al. also reported$^{[50]}$ an inorganic study to discover organic polymer photocatalysts for hydrogen evolution through the integration of their experimental results.

![Figure 10. Chemical structures of π-conjugated polymers.](Image)
and theory. Machine-learning exploring a sublibrary of more than 170 copolymers suggested the sacrificial hydrogen evolution rate of more than 6 mmol g\(^{-1}\) h\(^{-1}\).

A caution has been included in the papers\(^{[52]}\) on residual Pd-catalyst in the polymers. The \(\pi\)-conjugated polymers described above were usually synthesized via Pd-catalyzed polycondensation reactions, and the Pd-catalyst used strongly retained in the polymers, especially in crosslinked and networked ones, as metallic Pd particles or Pd clusters and was difficult to remove through classical purification. Studies of dependency of the metallic Pd particles or Pd clusters and was difficult to remove the polymers, especially in crosslinked and networked ones, as metallic Pd particles or Pd clusters and was difficult to remove through classical purification. Studies of dependency of the metallic Pd particles or Pd clusters and was difficult to remove.

Another breakthrough in such polymer suspension systems was also demonstrated in 2016 by Tian et al.\(^{[58]}\) who focused on \(\pi\)-conjugated polymers self-assembled and solubilized with block-polymer surfactants to form polymer dots (Figure 9c). Conjugated polymers 9 and 10 containing fluorene and benzo-thiazole units solubilized with poly(styrene-\(\beta\)-ethylene glycol), with diameters of 30–40 nm, in concentrated ascorbic acid solution (pH 4) yielded 8.3 and 50 mmol h\(^{-1}\) g\(^{-1}\) activities for hydrogen evolution when irradiated above 420 nm, respectively. The \(\pi\)-conjugated polymer dots are much smaller than suspended bulk polymers. Hence, the advantages for hydrogen evolution are: 1) The short migration distance of the photogenerated charges to the interface for electron injection that reduces protons, and the corresponding half-reaction of holes with the sacrificial reagent that suppresses charge recombination, and 2) a relatively large surface area for both hydrogen evolution and the half-reaction.

As shown above, conjugated polymers containing sulfone and benzo-thiazole units exhibited outstanding photocatalytic functionality, with polymers containing thiophene and ethynylene units delivering the second-highest activities. The reasons for these observations have been discussed, and include high exciton yields and/or their long lifetimes in the sulfone polymers, which is ascribable to the conjugated donor-acceptor structure, and the catalytic interactions between protons and the thiazole unit suggested computationally.\(^{[12a,54]}\) Conjugated polymers with network structures are highly porous and possibly suitable as large water interfaces, with widely delocalized \(\pi\)-conjugated structures for narrow bandgaps that absorb visible light and promote charge transfer through the 3D network. To realize this, dibenzo-thiophene dioxide was connected through pyrene units by Suzuki coupling to yield a conjugated porous polymer 11\(^{[55]}\) with a Brunauer–Emmett–Teller surface of 720 m\(^2\) g\(^{-1}\); its suspension in 20% aqueous triethanolamine delivered a hydrogen evolution rate of 5.7 mmol h\(^{-1}\) g\(^{-1}\) when irradiated above 420 nm. These studies into the photocatalytic water-reduction capabilities of metal-free-, \(\pi\)-conjugated polymer-catalysts suspended in aqueous solutions of sacrificial reagents provided the following insight into such polymers for water reduction applications:

1) Tuning the \(\pi\)-conjugated polymer structure is an effective approach toward both efficient visible-light absorption and exciton formation.

2) Electron injection to protons proceeds at the polymer surface, and its rate depends on the energy (potential) gap between the LUMO and the water reduction potential and/or (catalytic) interactions with protons at specific sites in these polymers.

3) A large excess of the sacrificial reagent is crucial in order to extract or completely consume holes in the polymers by the compensating oxidative half-reaction.

4) Large surface areas and microparticle, nanodot, or porous shapes enhance both the reductive and oxidative reaction rates of these polymers.

5) Nanodots reduce the charge-transport distance, and a networked \(\pi\)-conjugated system provides multiple pathways for charge transport.

However, a warning should be added regarding the analysis of the hydrogen evolution experiments. More specifically, the possibility of hydrogen produced by irreversible processes interfering the measured values. As noted in 2.5, sacrificial reagents are commonly irreversibly oxidized in the counter reaction, which may well involve hydrogen as one of the final products. In addition, some of the light-harvesting organic molecules (here being examined as a photocatalyst) often degrade over time, partially yielding hydrogen. Anyway, the use of a sacrificial reagent closes avenues for the practical development of these systems.

In relation to the above, the stoichiometric splitting of pure water into hydrogen and oxygen using a polymer powder is ideal because both photogenerated electrons and holes are used without the need for a sacrificial reagent to suppress the half-reaction. Until now, only one paper on conjugated polymer suspensions for total photocatalytic water splitting appears to have been reported. In 2017, Xu et al.\(^{[56]}\) prepared 1,3-dyne-linked polymers 13 with 1,3,5-tris(ethylphenyl)benzene units using cuprous-catalyzed condensation. The polymer exhibited a nanosheet-like morphology by transmission electron microscopy (TEM), with a high surface area due to the presence of both micro- and mesopores; its bandgap of 2.87 eV was ascribed to 2D conjugation. The LUMO and HOMO levels of 13 were found to be –3.00 and –5.87 eV, respectively, which are appropriate for water reduction and oxidation, respectively. Both hydrogen and oxygen were evolved with the expected 2:1 stoichiometry, with a hydrogen evolution rate of 218 µmol h\(^{-1}\) g\(^{-1}\) in pure water (pH 7) when irradiated. The apparent quantum efficiency and the solar-to-hydrogen conversion efficiency were measured to be 10.3% and 0.6%, respectively. While this work demonstrated the great potential of suspensions of well-designed conjugated polymers as unique photocatalysts for overall water-splitting applications, reports of their features compared against mainstream research using photocatalytic inorganic semiconductors are eagerly awaited.

In 2012, Antognazza et al.\(^{[57]}\) revived the conjugated polymer-based cathode concept by blending a conventional conjugated polymer with PCBM (phenyl-C61-butyric acid methyl ester) in a similar manner to bulk heterojunctions in photovoltaic cells. PCBM functions as an electron acceptor and mediates cascade-like electron-transfer from the excited electron in the LUMO of the polymer via the LUMO of PCBM for proton or water reduction. The 5/PCBM blend film on an ITO substrate was immersed as the photocathode in an aqueous saline (NaCl) solution, with the evolution of Cl\(_2\) at the wire-connected counter electrode monitored when illuminated. The same group reported the photocurrent of
<0.5 μA cm⁻² at 0 V versus RHE and pH 1.37, while the performance was improved by introducing a Pt catalyst and a MnO₂ hole-extracting layer on ITO.[60] Cheng et al. also used the 5/PCBM film on a poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS)-coated F-doped tin oxide (FTO) substrate to give the current of 45 μA cm⁻² at 0 V versus RHE under Xe irradiation, and developed it with a Pt catalyst and the combination with IrO₂ water-oxidation counter electrode resulting in the solar-to-fuel conversion efficiency of 0.12%.[69] Holdcroft et al.[60] restated in their 2018 study of 5-film-based photocathodes, including its photoelectrochemical study using anthraquinone reduction as a proton-reduction model and observed hydrogen evolution on the 5/PCBM-nanoparticle film.

Apart from polythiophenes, conjugated polymer 14 was synthesized, and its films tested as photocathodes for water reduction.[63] The donor–acceptor type copolymer 14, composed of carbazole and phenylenevinylene units, on FTO displayed a reduction current of 2.1 μA cm⁻² at 0.62 V versus RHE at pH 7 under 1-sun irradiation conditions.

In 2018, Feng et al.[62] reported the deposition of 12, which is a 2D diyne-linked 1,3,5-trithiophenebenzene prepared by Cu-surface-mediated polycondensation, on FTO and titanium substrates. TEM image showed that 12 has a 10 nm thick nanofibrous morphology, and a bandgap of 2.51 eV and a LUMO level of 4.12 eV, which are appropriate for visible-light absorption and proton reduction, respectively. A three-electrode system in aqueous Na₂SO₄ as the electrolyte at pH 6.8 under 1-sun irradiation conditions delivered a saturated cathode photocurrent of ~10 μA cm⁻² at 0 V versus RHE; an apparent quantum yield of 1.83% at 420 nm. Nanofiber morphology of the polymer upon a substrate (could be illustrated in Figure 9b) was discussed. The group modified 12 to 15 by introducing thienothiophene units, which delivered 21 μA cm⁻² under the same conditions. They suggested that either the nonsubstituted carbons of the benzene rings or the acetylenic carbons were the catalytic sites for proton reduction.

The same group[63] also further developed the diyne-linked triethynylenebenzene polymer 12 by incorporating diethylenylene and poly(1,4-ethynylbenzene) units in derivatives 16 and 17 (x = 0–0.1). The HOMO and LUMO levels continuously decreased (−5.17 → −5.85 eV and −2.73 → −3.41 eV) as the number of triphenylenebenzene units in 16/17 was increased (x = 0.02 → 0.1), respectively. A deeper HOMO level enhances the photovoltage and reduces the bias required to drive water-splitting. With this expectation, they prepared a gradient homojunction of 16 and repeat layers of 17, with x = 0.02 → 0.1. The open-circuit potential under illumination increased from 0.91 to 1.17 V versus RHE from 16 to the repeat layers or gradient homojunction photocathode; charge recombination was assumed to be suppressed in the given order. Consequently, the photocurrent increased from 19 to 55 μA cm⁻² for 16 on an FTO substrate to the 16/17 (x = 0.02 → 0.1) gradient when irradiated under 1-sun conditions with an applied potential of 0.3 versus RHE. The IPCE at 480 nm also increased from 1.7% to 2.8% in progressing from 16 to the 17 gradients. Gradient homojunction was claimed to enhance charge separation for photoelectric water reduction. The hydrogen evolution rate was correspondingly observed to increase to 0.94 μmol h⁻¹ cm⁻².

More recently, the same Feng group[64] used commercial Cu foam as a scaffold for cuprous-catalyzed polycondensations that yield polyenes. The catalytic effect of the Cu substrate was ruled out using control experiments. The thiophene-based linear polymer 21 had a deep HOMO level and a narrow bandgap of −5.23 and 2.17 eV, respectively, which could be ascribed to more delocalized conjugation due to the thiophene unit. A photoreduction current of 370 μA cm⁻² at 0.3 V versus RHE, an IPCE of 12.6%, a hydrogen evolution rate of 4.5 μmol h⁻¹ cm⁻², and a faradaic efficiency of >95% were recorded at pH 6.8. Calculations suggested that the Ce≡C bonds are activated toward water-reduction catalysis. The group searched for a Z-scheme heterojunction by incorporating the inorganic Cu₂O photocatalyst; that is, polymer 21 was formed on a Cu₂O-covered porous Cu substrate. A photocurrent of 520 μA cm⁻² was monitored at 0.3 V versus RHE, which is much higher than the 80 and 100 μA cm⁻² for 21 and Cu₂O, respectively.[65] The heterojunction suppressed charge recombination to deliver a carrier-separation efficiency of 16.1% at 0.3 V.

In 2019, Zhang et al.[66] reported a record activity value for the diyne-linked triethynylenebenzene polymer 12 as nanofibers formed in situ on a Cu foam substrate, namely 1.09 mA cm⁻², which is more than 100-times greater than the previously reported values at 0 V versus RHE when irradiated under 1-sun conditions. (Specific surface area of the Cu foam is >10² cm⁻², the reported current density per the cathode flat surface could be re-estimated).

Covalent organic frameworks based on π-conjugated building blocks as colored crystalline porous polymers were also examined as a photocathode material for water-reduction. Lotsch et al. synthesized the frameworks from the photoactive azine and pyrene linkers with the bandgap of 1.94 eV, which gave the photocurrent of 6 μA cm⁻² at 0 V versus RHE in 1 M H₂SO₄ under 1-sun irradiation.[68] Bein et al. reported the frameworks of benzothiophene and tetraaminophenylethylene, but their photocurrent remained at a few μA cm⁻².[69] The covalent organic frameworks were also studied for a photocatalytic water reduction by suspending in the aqueous solution of a sacrificial electron donor. Cooper et al.[70] developed their conjugated polymers of fused sulfones, 6 and 7, as the building block, and synthesized the framework by condensing diamino-bisbenzothiophene-sulfone with triformaldehydoroglucinol to yield the crystal with visible light absorption and hydrophilic mesopores. Its suspension in an ascorbic acid solution gave hydrogen evolution rate of 1.32 mmol g⁻¹ h⁻¹.

Graphitic carbon nitrides are another class of promising photoelectrical material for water-splitting applications; they are usually prepared through in situ deposition from gaseous starting components, function as n-type semiconductors, and have been mainly studied as photoanode materials, as recently reviewed.[71] Organic dye molecules, such as phthaloylamines, have been studied as photoelectrode materials in combination with, or as composites with inorganic semiconductors.[72] However, activity based on the dye was not high, and these hybrid photodecathodes are outside of the scope of this review.

Early trial studies using conventional π-conjugated polymers, and recent studies involving molecular design are presently concluded, with the following observations for efficient polymer-film-based photocathodes for light-driven water-reduction:

1) Molecular engineering approaches, such as the introduction of donor–acceptor conjugation and 2D conjugation networks,
are reasonable for narrowing HOMO–LUMO bandgaps for visible-light absorption and tuning LUMO levels such that they are appropriately shallower than proton- or water-reduction potentials.

2) While electron injection from the polymer surface to protons or water molecules proceeds driven by the energy-level or potential gap, specific functional group residues of the polymer presumably interact with protons and catalytically increase the rate of the reduction reaction.

3) An appropriately deep HOMO level is desirable in order to provide a satisfactory photovoltage and to reduce the bias voltage.

4) Gradient HOMO and LUMO levels from the water front to the substrate in contact with the polymer film contribute to enhancing the reduction current by layering a series of polymers and incorporating hole-transporting thin layers between the polymer film and the conducting substrate.

5) Substrates with large surface areas, such as that demonstrated using a Cu-foam substrate, increase the surface areas of the coated polymer film at both interfaces; i.e., for water reduction and hole-extraction by the substrate.

The primitive and most-representative π-conjugated polymers, namely polythiophene and its analogues, inherently satisfy conditions (1)–(3) and are being re-examined as photocathode films for water reduction by paying attention to untouched issues, such as exciton character, hole-mobility in the polymer, the electrostatic potential of the film surface, and electrolyte species, as discussed in Section 4.

4. Polythiophene Films and Their Photoelectrochemical Properties for Complete Visible-Light-Driven Water Splitting

One of the authors highlighted the redox nature of conducting polymers, such as PEDOT:P-toluenesulfonate, in his 2011 perspective paper. In these polymers work as electrocatalytic organic materials that reduce and completely remove oxygen from aqueous solutions through the formation of hydrogen peroxide and for water reduction. It was also addressed that conjugated polymers perform the dual functions of photoexcitation and electrocatalysis, and that polythiophenes seemed to be the most likely candidates for photoenhanced electrocatalysts for water reduction.

Surface polarization of a 5 film at the water interface when illuminated has been reported in molecular dynamics studies. Simulations revealed that the outermost layer of the polymer is negatively charged with photogenerated electrons and strongly attracts positive ions, such as Na\(^+\), from the electrolyte solution, thereby perturbing the homogeneous ion distribution. The use of 5 in 0.2 m aqueous NaCl was reported in the same paper to give a photocurrent of less than 10 \(\mu\)A cm\(^{-2}\) at +0.18 V versus RHE for water reduction. Bard et al. recently analyzed the photoelectrochemical properties of a 4 \(\mu\)m thick doped 5 film that was electrochemically oxidized and p-doped; irreversible doping was achieved by the incorporation of hydrophobic or bulky counteranions. The doped film on a FTO substrate was immersed in a benzoquinone electrolyte solution as the redox reagent in acetonitrile, which resulted in a doubling of the photocurrent compared to that of the undoped 5 film. The study highlighted that the controlled doping of 5 with relatively high carrier concentrations provides significantly higher photo-electrochemical performance and robustness than those of the pure 5 and of unintentionally impurity-doped 5. While the two studies discussed above are informative and provide some insight into the photocathode activities of polythiophene films, the activities remained very low for water reduction, or the film activity was only provided for nonaqueous systems. An approach that uses simple and unsubstituted polythiophene films instead of a 5 film bearing repeating hydrophobic hexyl substituents, is therefore advisable.

One of the current authors reported the preparation of poly(bithiophene) 22 films by vapor-phase polymerization using Fe(III) p-toluenesulfonate as the oxidizing agent on a glassy carbon substrate, with subsequent evaporation of bithiophene, washing with acid, and further cleansing with aqueous ethanol to completely remove residual iron. The 22-film-based cathode exhibited a reduced current density of 50 \(\mu\)A cm\(^{-2}\) at −0.19 V versus RHE at pH 6.9 when irradiated by a Xe lamp (onset potential of 0.27 V vs RHE), with a hydrogen evolution rate of 2.1 \(\mu\)mol h\(^{-1}\) cm\(^{-2}\) with a faradaic efficiency of 72%. Long-term durability testing showed successful operation over 12 d, with a corresponding turnover number of >6 \(\times\) 10\(^{4}\) without any chemical degradation observed by spectroscopic analyses, which strongly supports the superior chemical stability of the unsubstituted polythiophene film under continuous irradiation and repeated redox processes.

Adjusting the film thickness (0.1–1.2 \(\mu\)m) resulted in the most balanced hydrogen evolution at a thickness of 0.2 \(\mu\)m, despite the fact that a thickness greater than 0.4 \(\mu\)m is associated with greater UV–vis absorption, which is consistent with previously reported results for 5 films. Modifying the surface area of the 22 film is a way of improving the reaction rate at the interface, which was examined by preparing a porous film on glassy carbon and on a roughened surface; both gave higher photocurrents, but not markedly so. The effect of pH was studied in phosphate buffer solutions of pH 3–11, which revealed that the activity, even at pH 11 with an onset potential of 0.14 V, was below the theoretical reduction potential.

A mechanism for photocatalysis by polythiophene during water reduction was proposed by considering the dependency of the reduction current density on photo-intensity and wavelength, and examined by emission spectroscopy, in situ Raman spectroscopy, and DFT calculations. The following four steps were proposed: 1) Protonation at the sulfur atom of the photo-excited singlet state (S\(_2\)) thiophene residue, 2) subsequent excitation of the protonated intermediate via intersystem crossing to a long-lived excited triplet state (T\(_3\)), 3) the triplet intermediate, as a favorable species, reacts with surrounding protons or adjacent excited T\(_1\) intermediates to release hydrogen and to reform the corresponding cation, and 4) regeneration of the original thiophene residue through one-electron reduction and an applied potential via an external circuit.

\[
S \rightarrow S^+ \rightarrow S^2+ \rightarrow S^- \rightarrow S^- + H^+ \rightarrow (S^- + H^+) \rightarrow S^- + H_2
\]
or

\[
2(S - H^+) \rightarrow 2S^2^- + H_2 \quad (23)
\]

\[
S^+ + e^- \rightarrow S \quad (24)
\]

As an alternative scenario, the photoexcited thiophene residue is protonated, simultaneously reduced with an electron from the exciton or the applied potential, which spontaneously releases hydrogen

\[
2(S - H^+) \rightarrow 2(S - H) \rightarrow 2S + H_2
\]

These proposed mechanisms for photocatalytic water reduction using polythiophenes remain far from being confirmed because many of the encountered electrochemical and photochemical issues are associated with relatively small active species populations within the bulk film, and the complex nature of the heterogeneous catalyst. Despite this, the role of sulfur as a catalytic site and the importance of the photoexcited triplet states are key.

The authors successfully prepared unsubstituted and solvent-insoluble polythiophene (23) films in an in situ manner on a glassy carbon or FTO substrate without any contamination by trace-metal species.\[13\] A terthiophene solution was spin-coated on the substrate, which was exposed to iodine vapor (as the oxidant) to solid-state polymerize the terthiophene at 90 °C in a closed container (Figure 11a). The blue-black film of oxidized and polymerized terthiophene was repeatedly washed and reduced in ethanol and/or acetonitrile to give a deep-brown film without any residual iodine (I₂ and I⁻) or accidental metal contamination, as evidenced by X-ray photoelectron spectroscopy (XPS) and other spectroscopies. Doped or oxidized thiophene units in polymers have been known to act as electron traps for excited electrons. The electrical conductivity of the film was measured to correspond to that of an insulating semiconductor (only a few μS cm⁻¹), which clearly revealed the formation of completely undoped or reduced 23 films. The UV–vis spectrum of the film (Figure 11b) showed efficient visible-light absorption at below 640 nm, and provided values of 2.0, –5.2, and –3.2 eV for the bandgap and the HOMO and LUMO levels, respectively. The additional peaks at 520 and 590 nm (also observed in Figure 11b) are indicative of a π-interacting, highly ordered crystalline structure that is probably lamellarily packed in the film, as also suggested by X-ray fluorescence (XRF) (Figure 11c); such a structure had not been previously reported for electrochemically and oxidatively polymerized polythiophene films.

The 75 nm thick optimized film delivered a photoelectro-catalytic hydrogen production rate of 330 mmol h⁻¹ g⁻¹ in pH 7 phosphate buffer at 0 V versus RHE. The onset potential (vs RHE) for water reduction was more positive and the reduction current density at 0 V versus RHE increased with increasing electrolyte pH, which was unanticipated, with the highest value of 120 μA cm⁻² achieved at pH 11 (Figure 11b). The observed inverse Nernstian pH relationship warranted closer inspection. The electrical resistivity of the film was measured to be 6–9 MΩ in solutions of pH 4–12; the film was completely neutralized in alkaline solutions to facilitate charge transport in the film and photocatalytic activity. On the other hand, the current density at 0 V versus RHE was observed to decrease with increasing alkaline pH in the 11–13 pH range.\[14\] In addition, the LUMO level of the 23 is significantly shallower than the water reduction potential; consequently, the excited electrons already possess sufficient overpotential and may mask the pH dependency. It is possible that water, rather than protons, is the reactant on the film, which the alternative suggestion. In any case, such an apparent deviation from Nernstian pH dependency is noted not to be unusual for water reduction with a conjugated polymer film-based photocathodes.

The 23-film-based photocathode produced photovoltages greater than 900 mV for the hydrogen evolution reaction at pH 12, and is therefore suitably matched to traditional water-oxidation catalysts, such as MnO₂, CoO₂, and RuO₂ as counter anodes operating in alkaline solutions. A two-component electrochemical cell setup using the 23 photocathode and the MnO₂ catalyst on an FTO substrate as the anode was used to explore light-enhanced water splitting at moderate applied bias (Figure 13a). Hydrogen evolution rates of 24 and 0.45 mmol h⁻¹ g⁻¹ were observed at cell biases of 1.23 and 0.3 V, respectively.

Molecular designs that deepen the HOMO level of the polyterthiophene film are effective for promoting facile water-splitting without the need for an applied potential bias. The authors introduced an electron-withdrawing phenylene repeating unit in the polythiophene backbone by the in situ polymerization of dithienylbenzene with iodine vapor as the oxidant.\[13\] The resulting 24 polymer has HOMO and LUMO levels that were lowered by 0.3 and 0.1 eV, respectively, compared with those of 23 (Figure 13), and delivered a reduction current of 128 μA cm⁻² at 0 V versus RHE with...
an onset potential of 1.0 V versus RHE at pH 11 when illuminated; the hydrogen evolution rate of 2.5 mmol h$^{-1}$ g$^{-1}$ was measured with a faradaic efficiency of 89%. The illuminated open circuit potential of 1.38 V versus RHE at pH 12 is sufficient for water reduction, and a hydrogen evolution rate of 2.5 mmol h$^{-1}$ g$^{-1}$ was recorded at 1.24 V versus RHE. A two-compartment 24-photocathode/MnOx-anode setup delivered a hydrogen evolution rate of 6.4 mmol h$^{-1}$ g$^{-1}$ without any applied potential; the rate increased to 18.3 mmol h$^{-1}$ g$^{-1}$ when a low bias voltage of 0.1 V was applied.

The introduction of an electron-withdrawing phenylene unit in the polythiophene backbone lowered the HOMO level but resulted in a widening of the bandgap or a blueshift in the visible absorption edge. More appropriate tuning of the HOMO and LUMO levels for both water reduction and oxidation, respectively, and for more-efficient visible-light absorption is still anticipated. The authors recently successfully prepared a neat film of unsubstituted and solvent-insoluble polythiophene (23') in a facile manner, which absorbed at up to 640 nm visible region, with HOMO and LUMO energies of −5.43 and −3.27 eV, respectively. The film was characterized with an uniquely well-filled grain morphology of the crystalline polymer, which provided a very high photoelectrocatalytic hydrogen evolution rate of almost 1 mA cm$^{-2}$ and a high photovoltage (>1.23 V vs RHE). In situ polymerization of the terthiophene layer in the presence of a miscible but removable additive molecule using iodine vapor as the oxidant produced thin polythiophene film with well-filled polymer grains that were larger than 50 nm and stretching across the thickness of the produced film; a cross-sectional scanning electron microscopy (SEM) image is shown in Figure 14a,b. The impedance spectrum of the film immersed in water showed very low electrical resistance, which supports the unique vertical morphology that connects the film/water interface to the substrate surface through single large polymer grains. The polythiophene film was shown to contain a predominantly planar crystal structure by XRD (Figure 14c), and exhibited an emission peak at a significantly high wavelength, as is evident in the spectrum in Figure 14d. These observations are consistent with decay from a triplet state resulting from the increased planar, π–π stacked, conjugated, and delocalized structure. The existence
of a preferred triplet state supports the significant extended lifetime of the excited species and the diffusion length of the exciton, which presumably reaches the film/water interface (see Figure 5).

The $23'$ film-based photocathode immersed at pH 12 exhibited a high reduction current density ($>0.7$ mA cm$^{-2}$ at 0 V vs RHE) when irradiated with a 300 W Xe lamp (Figure 15a). Gas chromatographic monitoring of hydrogen gas evolution (Figure 15a) provided a gravimetric photoelectrocatalytic conversion rate of 1.02 mol H$_2$ h$^{-1}$ g$^{-1}$, with a faradaic efficiency of $>95\%$, which was higher than those of previously reported photocatalysts and at least 100 times higher than those of inorganic semiconductors. The film exhibited a very high open-circuit potential of 1.38 V versus RHE at pH 12 when illuminated (Figure 15b), which exceeds the theoretical potential of 1.23 V. The obtained photovoltage was sufficient to drive water electrolysis to completion when irradiated with visible light in a one-photon-per-electron process. A two-compartment cell without separator in an illuminated setup composed of the $23'$ photocathode and a MnO$_x$ catalyst anode at pH 12 delivered a hydrogen evolution rate of 3.2 mmol h$^{-1}$ g$^{-1}$ at no applied bias, and excellent durability (Figure 15c).

The neat polymer film was robust for long-term reductive reactions, which is ascribable to the chemical stability of the unsubstituted and solvent-insoluble polythiophene as well as strong adhesion of the in situ polymerized film that avoids separation from the conducting substrate. The smooth flat film surface, rather than a porous surface, afforded very high catalytic activity per bulk photocathode surface area (cm$^{-2}$); fortunately, this also suppressed hydrogen-adsorption or the accumulation of the produced microbubbles at interface.

Performances of various polymer film-based photocathodes, in terms of the photocurrent density and the photovoltage, are shown at a glance in Figure 16.

5. Light-Driven Reduction of Oxygen to H$_2$O$_2$ on Conjugated Polymer-Based Photocathodes

As shortly introduced in Section 1, the light-driven photochemical production of H$_2$O$_2$ from oxygen has also been studied using organic powders as a metal-free semiconductor photocatalysts suspended in water in the presence of oxygen. Organic dyes and lignins have been investigated as a photocatalyst of oxygen reduction to H$_2$O$_2$ usually in the presence of a sacrificial reagent, such as oxalate and formate.$^{[78]}$ Shiraishi et al.$^{[79]}$ prepared resorcinol-formaldehyde resin (25) as a reddish-orange
power with an average particle diameter of ≈1 µm, with HOMO and LUMO energies of 2.21 and 0.21 V versus RHE (0.1 m KCl), respectively, and a narrow bandgap of 2.0 eV that was ascribed to π-stacking of benzenoid–quinoid donor–acceptor couples. While a 0.5% solar-to-chemical conversion efficiency of the powder in deionized water under under 1 sun illumination was the highest among those reported for powder-type inorganic photocatalysts, the H₂O₂ production rate was a low of 3 mg H₂O₂ g⁻¹ photocat h⁻¹.

Photoelectrocatalysts or photocathodes for the reduction of oxygen to H₂O₂ have also been investigated with the aim of achieving higher catalytic rates when illuminated in the presence of an additional bias potential. Typical examples in this regard include the organic epindolidione pigments reported by Glowaski et al. [23a] and the dye-sensitized nickel oxides by Mayer et al. [23b]. Although the H₂O₂ production rates exceeded those of previous photocatalysts by one-to-two orders of magnitude, the corresponding devices usually required bias voltages. Toward practical use, a photoelectrocatalytic cell for H₂O₂ production was proposed. [81] In most cases, such a combination requires the use of different electrolytes for the anode and cathode compartments. Glowaski et al. recently reported a similar approach to the photoelectrochemical production of H₂O₂ using a combination of phthalocyanine, perylene carboxylic imide, and gold as a complexed and unsteady photocathode and a Nafion membrane as the separator. [81b]

The reduction potential for the conversion of oxygen to H₂O₂ is much more positive or deeper than that for water reduction; hence oxygen reduction proceeds favorably and with high faradaic efficiency ahead of water reduction in oxygen-containing aqueous solutions when a negative potential is applied, irrespective of H₂O₂-formation selectivity. Polythiophenes have been studied as organic electrocatalysts for the reduction of oxygen to H₂O₂ in the dark [8,82]. The reduction current density of a polythiophene-based cathode attributed to the oxygen-reduction reaction largely depends on the oxygen solubility in water [83] and is therefore usually at the sub-mA cm⁻² level, with overpotential decreasing with increasing solution pH and approaches zero versus the standard equilibrium potential at pH 12. A high pH was found to be beneficial for electrocatalytic activity, which suggested that protons are not involved in the reaction, and that oxygen and water are the reactants, as described by Equations (14) and (15). HO₂⁻ is regarded as equivalent to H₂O₂, as HO₂⁻ formed in alkaline solutions [84] is more stable than H₂O₂ at pH 7 (e.g., the half-lives of HO₂⁻ (pH 12) and H₂O₂ (pH 7) are 1.2 months and 48 h, respectively). In an alkaline solution, HO₂⁻ is readily converted into highly reactive H₂O₂ by facile neutralization. This aspect is another advantage.
of oxygen reduction at high pH for the practical production of H2O2 on-site.

The authors synthesized the copolymer of phenylene and thiophene 24 and analyzed first the 24-film\(^\text{[85]}\) as an electrocatalyst for the reduction of oxygen to H2O2 or HO2\(^-\) in the dark. In situ Raman spectroscopy of 24 revealed charge transfer through the phenylene groups of 24 as the catalytic sites after the application of a potential, consistent with a two-electron reduction per repeating unit in the presence of oxygen. While thiophenes have often been reported to be the catalytic active sites for H2O2 production,\(^\text{[82a,86]}\) this experimentally proposed mechanism suggests that a benzene moiety is a more favorable site for catalytic H2O2 production than a thiophene, presumably due to the resonance stability of the intermediate formed. The high stability of the intermediate may support the high catalytic ability of 24 at high pH, which highlights the potential of molecularly designing more efficient and robust aromatic polymers as photocatalysts. Charge transfer through catalytic sites on the phenylene groups follows a completely different catalytic route to that involved in the light-promoted reduction of water to H2 (on the thiophene groups) described in Section 3 and 4 for \(\pi\)-conjugated polymers.\(^\text{[76]}\)

The authors examined a cathode using a 210 nm thick 24 film for H2O2 production under light at high pH with air bubbling through the solution (oxygen/nitrogen gas mixture). A H2O2-production rate in excess of 40 g H2O2 g photocat\(^-1\) h\(^-1\) with a faradaic efficiency of 96% was observed at pH 12. Long-term durability testing under illumination at +0.91 V versus RHE showed remarkable robustness for 1 week, with a turnover number exceeding 10\(^5\) and high reproducibility. Analysis of the polymer film did not show any change in the chemical composition of 24 over the week-long experiment.

The HOMO level of 24 (\(-5.5 \text{ eV}\)) is deeper than the water-oxidation potential at high pH. The onset potential for oxygen reduction with the 24 film under light was 1.53 V versus RHE at pH 12, which significantly exceeds the +1.23 V versus RHE water-oxidation potential and is sufficient to concurrently drive water oxidation on the anode without any additional bias, resulting in a one-photon-per-electron reaction in the overall system.

These unique properties of the 24 film make it suitable for combining with a traditional high-pH water-oxidation catalyst, and a two-component cell was used to explore light-driven H2O2 production at zero applied bias; the MnO\(_x\) water-oxidation catalyst on an FTO plate was used\(^\text{[87]}\) as both counter and reference electrodes (Figure 17a). A separate experiment revealed that the MnO\(_x\) electrode does not oxidize H2O2 under the alkaline conditions used, rather it simply provides additional oxygen for the production of H2O2. Time-course monitoring of accumulated charge at 0 V bias (Figure 17b) clearly revealed current flow between the two half-cells, thereby confirming the ability of 24 to produce a photovoltage sufficient for water oxidation on MnO\(_x\). H2O2 (or HO2\(^-\)) production was also quantified (Figure 17b) and shown to coincide with the amount of charge flow, leading to a faradaic efficiency of \(>95\%\). The 24 film delivered an outstanding H2O2 production rate of 11 g H2O2 g photocat\(^-1\) h\(^-1\), even without a bias voltage.

Very recently, Li et al.\(^\text{[88]}\) reported a record-high H2O2 concentration of 0.11 M after photocatalytic oxygen reduction involving electro-polymerized polyterthiophene for 11 h at high pH. A dual-photoelectrode cell was also developed using

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**Figure 17.** a) A tandem photoelectrochemical cell without any separator and in the absence of a bias potential at pH 12 with the photoirradiated 24-film cathode and the MnO\(_x\) anode. b) Accumulated charge over time (solid line) upon illumination at zero bias versus MnO\(_2\) at pH 12 and H2O2 production (plots) upon the illuminated 208 nm thickness 24-film.
polythiophene, NiFeO₂ and BiVO₄ as water-oxidation photocatalysts, and a Nafion membrane. On the other hand, the 24-film photocathode, with sufficient photovoltage to drive both the anode and cathode reactions, eliminated the need for different electrolytes and a membrane separator between the two compartments.

Although a simple two-compartment setup (Figure 17a) is advantageous as a measuring system, it is limited in terms of electrolyte resistance and the external circuit. To significantly reduce energy loss related to these factors, a simpler and more-direct combination of the 24 film and MnOₓ was subsequently implemented, in which MnOₓ was electrodeposited on one face of an electrically conductive thin plate, and a 24 film was then formed on the opposite face of the same plate. The performance of the 24 photocatalyst combined with MnOₓ in this manner at pH 12 under 1.0-sun irradiation conditions (see the right figure in the Table of Contents) gave an outstanding H₂O₂ production rate of 14 g H₂O₂ g photocat −1 h −1 or 0.20 mg H₂O₂ cm⁻² h⁻¹, which was maintained for over 1 week.

Currently, the authors prepared transparent plates composed of electrically conducting plastic substrates sandwiched by 24 films and MnOₓ layers, which was tested for the production of more-concentrated H₂O₂ by illuminating five-layer-stacked plates soaked in alkaline water (Figure 1b). [25] The plate combined with the 24 photocatalyst and MnOₓ was easy fabricated and did not require any separators or membranes in the water pool, making it highly suitable for practical use. A steady H₂O₂ production rate of 14 g H₂O₂ g photocat −1 h −1 was achieved with this setup. Therefore, the developed photocatalyst is a simple, sustainable, and safe H₂O₂ production material that meets the rapidly growing demand for decentralized H₂O₂ production and use.

The LUMO level (−3.3 eV) of 24 is more than 1 V shallower than the theoretical potential required for the conversion of oxygen into H₂O₂ at high pH, which leaves ample room for the design of phenylene/thiophene polymers with deeper-lying LUMOs and, hence, narrower bandgaps, in order to harvest longer wavelengths from the solar spectrum.

6. Short Summary and Perspectives

This article surveyed research, spanning nearly four decades including ones that have remained dormant for a long but have recently been re-examined, into photocathode-active organic materials, that is, π-conjugated polymers that can drive the solar-light reduction of water to produce hydrogen gas or hydrogen peroxide. The polymers function as photo(electro)chemical catalysts in the forms of film, layers, or coatings on current-collecting plates or substrates, which is ascribable to the inherent advantages associated with moldable polymers, leading to simple, additive reagent- and separation-free processes compared to those using inorganic photocatalyst particles and polymer suspensions, thereby providing ultimate green hydrogen and hydrogen peroxide energy sources from on-site water.

Extensive studies into photocathode films composed of single-component conjugated polymers achieved first benchmark values after tuning the preparation and measurement conditions; that is, a photoreduction current density of 1 mA cm⁻² and production rates of 1 mol H₂ h⁻¹ g photocat⁻¹ and 1 g H₂O₂ h⁻¹ g photocat⁻¹, some of which have activities that are comparable with those of inorganic semiconductors. Very high open circuit potentials that exceed the theoretical potentials of 1.23 and 0.70 V for water splitting and oxygen reduction to H₂O₂, respectively, demonstrate the possibility of one-photon-electron processes that enable bias-free and self-standing systems to be fabricated for hydrogen and hydrogen peroxide production from water when irradiated by sunlight (as illustrated in the figures in the Table of Contents).

However, there remains significant room for performance improvement; for example, systems that deliver more than 10 mA cm⁻² and can be used in practical devices for water-splitting and H₂O₂-production applications. Further design and tuning is desirable into polymer materials, film-water interface, film configuration, and cell or device structure, which are shortly addressed below in this order.

The requirements of conjugated polymers as a photocathode material for water and oxygen reductions were described in this article by referring to previously reported results, including research using polymer powder suspensions. An appropriate LUMO level sufficient to drive reductive reactions at the water interface, an appropriate HOMO level to provide a high photovoltage, and a narrow HOMO–LUMO gap for visible light absorption are the first requirements. The balanced positions are recommended, at the present, to be the LUMO level of −3.3 eV for hydrogen evolution reaction (≈3.8 eV for oxygen reduction to H₂O₂), the HOMO level from −5.3 to −5.4 eV for catalytic oxygen evolution, and the bandgap of 2.1 eV for visible-light absorption up to 600 nm. While these band positions or energy levels are interlinked, the alignment could be tuned by molecular designing of the polymer, such as, a slightly deep HOMO level by introducing an electron-withdrawing unit in the polymer to enhance the photovoltage. The formation of sufficient excitons and their diffusivity, efficient hole migration in the polymer film, and efficient hole extraction at the substrate interface, are also required. Crystalline structure in the π-conjugated polymer could facilitate the exciton formation and its diffusivity to increase the injection rate of electrons for the reductive reactions at water interface. p-Doping or hole-generation in the polymer occasionally help the hole-conduction in the film, but it often traps excited electrons. Analysis on the position of a p–n junction front or a rate-determining step in the operating polymer film would be welcomed.

In addition, the reductive reaction mechanism at the water front has not yet been experimentally analyzed and is still an open question; whether it involves single electron injection into water and/or oxygen, with driving force based on the energy gap, or a kinetic but chemical pathway is unclear. Electrochemical kinetic and equilibrium studies in the dark that enable parameters to be measured, such as the electrode potential and the exchange current density between the cathode and the reactant in water, are awaited for deeper understanding of the photocathode working process.

Designing of the photocathode-films enables further development. Multiple layers of light-harvesting, hole-transporting and -extracting, and water-front catalytic functioning material can be stacked on a substrate or current-collecting plate. Film thickness can be tuned to balance light-absorption and the diffusion lengths of excitons and holes. A couple of photocathodes formed using a transparent ITO or FTO plate and two polymers with wide and narrow bandgaps, respectively, can absorb over a wide wavelength range in a tandemly configured cell. Hole-extracting
thin layers are crucial to avoid kinetic saturation of the current density and/or to suppress charge-recombination for widening the photovoltage. Thin layer materials could be selected along the energy level positions of HOMO of the conjugated polymer layer and of the substrate material. Introduction of a coelectrocatalyst, such as Pt and Pd, in the surface contacted with water is a quick avenue to improve the hydrogen evolution rate in combination with the light-harvesting conjugated polymer under acidic conditions[9a,89] (however, it was outside the scope this article).

Polymer films with large surface areas in contact with water, which are associated with porosity, hydrophilicity, and wettability, are desirable. The surfaces of the cathode polymer films were determined to be negatively charged, and are balanced by excess cationic species in, or departing anionic products from the electrical double layer where pH as well as electrolyte species likely influences reactivity. The real cathode reaction involves many processes, including adsorption of water, protons or oxygen, electron-transfer, bond cleavage and rearrangement, and the desorption of hydrogen or H₂O₂ and their activation energies, which are also affected by mass-diffusion processes and solution stirring, among others; all of these factors determine cathodic-reaction efficiency. These mechanisms and factors operating during water and oxygen reduction have scarcely been studied for organic-based cathodes. Engineering of three layers and of the substrate material. Introduction of a coelectrocatalyst, such as Pt and Pd, in the surface contacted with water is a quick avenue to improve the hydrogen evolution rate in combination with the light-harvesting conjugated polymer under acidic conditions[9a,89] (however, it was outside the scope this article).

Among similarly designed \( \pi \)-conjugated polymers, light-driven oxygen evolution from water, as the counterpart to water splitting, remains an important challenge. Photocatalytic chemical functions of conjugated polymers have also been promoted by their other applications in aqueous interfaces, mainly in the field of sensors and biotechnology.[10,91] Conjugated polymers are chemically stable and mechanically tough during long-term redox operations in water with a wide range of pH values; they are nontoxic, inexpensive, and nonlimited resource materials. Conjugated-polymer-film-based photo(electro)chemical processes hold great potential for both compact on-site, and durable and scalable solar-fuel-generation applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

hydrogen peroxide production, organic thin films, photoelectron conversion, water splitting, \( \pi \)-conjugated polymers

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