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Review Light-driven water oxidation for solar fuels

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Abbreviations: Acac, acetylacetonate; BODIPY, boron-dipyrromethane; bpmp, 2,6-bis[[N,N-di(2-pyridylmethyl)amino]methyl]-4-methylphenol; bpp, bis(2-pyridyl)pyrazolato; bpy, 2,2-bipyridine; bpy-Mebim₂py, 2,2'-(4-methyl)-[2,2':4',4"-terpyridine]-2"-6"-diyl-(bis(1-methyl)-1H-benzo[d]imidazole); Cp*, 1,2,3,4,5-pentamethylcyclopentadienyl; D- π -A, donor-pi-acceptor; DC, direct current; DFT, density functional theory; DSSC, dye-sensitized solar cell; EPR, electron paramagnetic resonance; FITC, fluctuation-induced tunneling conduction; FTO, fluorine-doped tin oxide; GC-MS, gas chromatography-mass spectrometry; HOMO, highest occupied molecular orbital; IPCE, incident photon-to-current conversion efficiency; ITO, tin-doped indium oxide; LUMO, lowest unoccupied molecular orbital; MLCT, metal-to-ligand charge transfer; NHE, normal hydrogen electrode; OEC, oxygen-evolving complex; PCET, proton-coupled electron transfer; PSII, photosystem II; PVP, poly(4-vinylpyridine); salen, N,N-ethylenebis(salicylimine); tacn, 1,4,7-triazacyclononane; tpy, 2,2':6,2"-terpyridine; t-tpy, 4'-(p-pyrrolylmethylphenyl)-2,2':6,2"-terpyridine; TW, terawatt; UV, ultraviolet; VCS, vitreous carbon sponge; XRD, X-ray diffraction.

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ABSTRACT

Light-driven water oxidation is an essential step for conversion of sunlight into storable chemical fuels. Fujishima and Honda reported the first example of photoelectrochemical water oxidation in 1972. In their system, TiO₂ was irradiated with ultraviolet light, producing oxygen at the anode and hydrogen at a platinum cathode. Inspired by this system, more recent work has focused on functionalizing nanoporous TiO₂ or other semiconductor surfaces with molecular adsorbates, including chromophores and catalysts that absorb visible light and generate electricity (i.e., dye-sensitized solar cells) or trigger water oxidation at low overpotentials (i.e., photocatalytic cells). The physics involved in harnessing multiple photochemical events for multi-electron reactions, as required in the four-electron water-oxidation process, has been the subject of much experimental and computational study. In spite of significant advances with regard to individual components, the development of highly efficient photocatalytic cells for solar water splitting remains an outstanding challenge. This article reviews recent progress in the field with emphasis on water-oxidation photoanodes inspired by the design of functionalized thin-film semiconductors of typical dye-sensitized solar cells.

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1. Introduction

The quest for abundant, renewable energy is currently one of society's greatest technological challenges. Light energy from the sun strikes the earth's surface at a continuous rate of 1.2×10^5 TW, vastly exceeding our current worldwide power demand of 17 TW (1 TW = 10^{12} J/s) [1]. Though solar energy is plentiful and globally distributed, it is also intermittent and diffuse. One solution for these problems is the conversion of light energy to storable chemical fuels, including H₂ or reduced carbon compounds [2,3].

Whatever the form of the fuel, reducing equivalents—protons and electrons—will be needed for its production. Water is the most abundant feedstock for obtaining these reducing equivalents. However, efficient water splitting is regarded as one of the barriers to the development of solar fuels technology. Water oxidation, shown in Eq. (1), is necessarily energetically demanding but has the advantage of conceivably storing large amounts of energy by producing electrons for fuel-forming reactions. The process is also mechanistically complex, requiring a catalyst to minimize the overpotential.

$$2H_2O \to O_2 + 4H^+ + 4e^- \quad E^\circ = 1.23 \, V \tag{1}$$

In photosynthesis, nature provides a model for harvesting solar energy to produce reducing equivalents from water. In the enzyme photosystem II (PSII), light-induced charge separations sequentially oxidize a Mn_4CaO_x cluster known as the oxygen-evolving complex (OEC). After the fourth oxidation step, dioxygen is released [4]. Although the release of oxygen is merely a byproduct from the point of view of solar fuel production, it is a central process in ensuring that the atmosphere remains oxygen-rich, a factor that is in turn necessary for the combustion of any fuel. The water-derived protons and electrons are ultimately used to fix carbon dioxide and produce biomass. Photosystem II operates with an overall energy storage efficiency of 46% using 680 nm photons and produces oxygen at a maximum rate of 50 s^{-1} [5].

The first example of photoelectrochemical water splitting was reported by Fujishima and Honda in 1972 [6]. In their system, a titanium dioxide (TiO₂) photoanode was irradiated with ultraviolet light, producing oxygen at the anode and hydrogen at an unilluminated platinum cathode. Since 1972, many groups have attempted to modify this system to use visible instead of UV light, and many of these systems share common components, shown in Fig. 1. In general, a molecular chromophore is coordinated to the surface of a wide band gap semiconductor, most commonly TiO₂. A long-lived charge separation is established when the semiconductor conduction band accepts an electron from the photoexcited chromophore [7]. A catalyst covalently bound to the chromophore or functionalizing the semiconductor surface donates an electron to regenerate the starting chromophore from the cation radical formed in the initial transfer step. After four successive charge separation events, the catalyst releases oxygen. While the steps of this scheme are relatively straightforward, integrating efficient visiblelight absorption, stable charge separation, and fast water-oxidation catalysis is much more complicated. These problems are far from solved, and much effort has been devoted to the design, synthesis, spectroscopy, and computational study of these systems.

Here we review the parallel development of the preparation of light-harvesting molecules coupled to semiconductor surfaces, understanding of the relevant photochemical and electrochemical processes and the nature of charge transport in the host semiconductor material, and catalysts capable of completing the four-electron water-oxidation reaction. We also discuss the progress made to date in the design and construction of functional water-oxidation photoanodes.

2. Design and assembly of photoanodes

While inexpensive and abundant, TiO_2 is a wide band gap (~3.2 eV) semiconductor that does not absorb light in the visible



Fig. 1. A proposed device for the production of solar fuels by visible-light-driven water oxidation.



Fig. 2. Anchoring groups for binding molecular species to titanium dioxide: (A) carboxylic acid, (B) phosphonic acid, (C) hydroxamic acid, (D) 3-substituted-2,4-pentanedione (acetylacetonate), and (E) catechol.

region [6]. Grätzel and coworkers developed a dve-sensitized solar cell (DSSC) in which visible light can be converted to usable electric current by separating the roles of visible-light absorption and charge transport [8–10]. In a typical DSSC, a molecular dye is covalently bound to a nanoporous TiO₂ thin film, and upon photoexcitation with visible light, electrons are injected into the conduction band of the semiconductor. These electrons flow to a counter electrode where a redox-active species in the electrolyte solution completes the circuit by accepting the electrons and transporting them to the anode where they reduce the photooxidized dye. The most effective DSSCs reported to date are based on a ruthenium-polypyridyl dye with overall conversion efficiencies of up to 11.2% when assembled with N719 on TiO₂ and $I^-/I_3^$ in acetonitrile as the electrolyte [11] or otherwise based on a specialized porphyrin dye with 12.3% efficiency when deposited on TiO₂ and using $[Co(bpy)_3]^{2+}/[Co(bpy)_3]^{3+}$ electrolyte [12]. The development of DSSCs has been extensively reviewed elsewhere and is not covered here [9,10,13].

In solar photocatalytic cells inspired by DSSCs, visible-light absorption and charge transport is fulfilled with photoanodes based on a semiconductor thin film sensitized with suitable chromophores. Rather than generating current, the photoanode drives water oxidation through the incorporation of a suitable catalyst. A redox electrolyte is no longer needed; instead, water is reduced at the cathode and oxidized at the anode. An appropriate photosensitizer should exhibit broad and intense absorption in the visible region, maintain strong attachment to the surface, and promote efficient charge separation. In order to drive the water-oxidation chemistry, the oxidized photosensitizer should give a thermodynamic reduction potential more positive than the onset potential for catalytic water oxidation plus the overpotential required by the catalyst. The catalyst should be in close proximity to the chromophore to allow it to couple the water-oxidation catalysis efficiently to the photochemistry. Although the anode is typically considered the photoactive side of such a photoelectrochemical cell, devices with a photocathode or with both electrodes being photoactive cannot be excluded from consideration for future work.

2.1. Anchoring groups for photosensitizers or catalyts

In early attempts at sensitizing TiO_2 to visible light, dyes were weakly adsorbed onto the surface. Stronger bonds between the sensitizers and the surface offer increased surface coverage and stronger electronic coupling between the occupied orbitals on the dye and the conduction band of the semiconductor, leading to improved stability and performance [9,14]. Numerous anchoring groups including catecholates, carboxylates, phosphonates, acetylacetonates, and hydroxamates, shown in Fig. 2, have been employed to bind photoactive and redox-active molecules to metal oxide surfaces. Suitable anchors for a water-splitting photoanode must provide strong chemical adsorption between the molecular species and the bulk surface and should also be stable under both aqueous and oxidative conditions. Of particular interest are anchoring groups that offer robust surface attachment of light-harvesting chromophores and also facilitate fast and efficient electron injection from the photoexcited dye to the conduction band of the semiconductor. A water-oxidation catalyst may also be anchored directly to the semiconductor surface. In general, the same anchoring groups may be used for either photosensitizers or catalysts.

2.1.1. Carboxylate and phosphonate anchors

Carboxylic acids (–COOH) and phosphonic acids (–PO(OH)₂) have been studied for the attachment of molecular species to TiO₂, perhaps owing to their synthetic accessibility [15]. The majority of the effort has focused on binding ruthenium–polypyridyl photosensitizers to TiO₂.

Phosphonate groups have been shown to afford stronger bonds to TiO₂ than carboxylates. For a sensitizer of the form $[Ru(bpy)_2(4,4'-(Q)_2bpy)]^{2+}$, where Q = anchor, the adduct formation constant for a phosphonate complex on TiO₂ was an order of magnitude greater than for an analogous carboxylate complex, suggesting the phosphonate linkage to TiO_2 is stronger [16]. Similarly, a ruthenium complex with a phosphonate-functionalized terpyridine ligand had a binding constant to TiO_2 that was ~80 times greater than for the carboxylate complex under similar conditions [17]. The relative adsorption strength of carboxylic acid and phosphonic acid anchor groups to TiO₂ has also been investigated using density functional theory (DFT) calculations. Phosphonic acid was found to bind substantially more strongly than carboxylic acid to TiO₂, based on calculated adsorption energies [18]. However, it is important to note that the predicted rate of electron injection from the carboxylate-anchored isonicotinic acid to TiO₂ was twice as fast as from 4-pyridyl phosphonic acid [18], as discussed in Section 3.2.

While phosphonate anchors bind more strongly to TiO_2 in aqueous solvents than do carboxylates, the relative stability of the anchors under the actual operating conditions of the system must also be considered. Anchors to a photoanode for light-driven water splitting also need to be stable under oxidative conditions. Surface desorption studies of ruthenium sensitizers in aqueous solutions at pH 5.7 showed 90% desorption when a carboxylate anchor was used compared to only 30% desorption for a phosphonate anchor under the same conditions [16]. This suggests that, of the two, phosphonates might be more suitable anchors than carboxylates in water-splitting cells, despite their less efficient electron injection.

The number of functional groups employed to bind bulky ruthenium-polypyridyl complexes to TiO2 also affects the stability and performance of the sensitizer. Studies comparing the efficiency of DSSCs made with ruthenium-phenanthroline photosensitizers with varying numbers of carboxylate anchors showed increased efficiency when two or more carboxylate anchors per chromophore molecule were employed [19]. Studies comparing analogous ruthenium-tris(bipyridine) complexes, functionalized with either carboxylate or phosphonate groups on one, two, or all three of the bipyridine ligands, again showed not only that the number of anchors employed affects DSSC efficiency but also that the trends depend on the type of anchor employed [20]. With phosphonate anchors, surface binding was strong enough such that the presence of additional anchors did not greatly influence adsorption strength, and DSSC efficiency was correlated to the molar absorptivity value, which increased with the number of electronwithdrawing phosphonate groups [20]. The efficiency of sensitizers with carboxylate anchors was not directly correlated with molar absorptivity but was instead governed by the stability and binding mode of the carboxylate anchors, such that four anchors were



Fig. 3. Ruthenium-tris(bipyridine) complexes with one bipyridine ligand functionalized with either phosphonate anchors (left) or methyl-phosphonate anchors (right).

better than two or six [20]. The authors suggest that four anchors provide a balance between robust coordination through anchoring groups on two different bipyridine ligands while suppressing the aggregation between carboxylate groups that are not bound to the surface. In general, these studies provide design principles that indicate that each type of anchoring group requires a separate optimization procedure.

Direct attachment of an anchor group to a chromophore has also been shown to improve photocurrent efficiency and electron injection quantum yield relative to an anchoring group that includes an alkyl spacer. For example, the addition of a methylene group between a phosphonate anchor and a bipyridine ligand in a ruthenium-polypyridyl chromophore significantly changes the properties of the sensitizer (Fig. 3) [16]. The half-wave reduction potential of the Ru^{II/III} couple for the phosphonate (–PO(OH)₂) complex is about 100 mV more oxidizing than for the more electron-donating methylene phosphonate (-CH₂PO(OH)₂) substituent. The electron-withdrawing nature of the phosphonate group lowers the energy of the bpy π^* orbital and lowers the energy of the metal-to-ligand charge transfer (MLCT) excited state leading to a red shift in λ_{max} , but only in the absence of the methylene group. The effect of alkyl spacers on electron-transfer processes is discussed in more detail in Section 3.2.1.

2.1.2. Hydroxamate, acetylacetonate, and catecholate anchors

A variety of other anchor groups including hydroxamates, acetylacetonates, and catecholates have also been explored for the covalent attachment of sensitizers and catalysts to TiO₂. Hydroxamate anchors (Fig. 2C) provide water-stable attachment of molecular species to TiO2 and exhibit favorable electron-transfer characteristics [21-23]. Binding enthalpy calculations suggest that species bound with hydroxamate or carboxylate anchors would exhibit similar interfacial electron transfer but that the hydroxamate anchor would be 33% more stable than a carboxylate anchor on anatase TiO₂ [21]. Experimental data comparing analogous organic azo dyes with hydroxamate or carboxylate anchors support these predictions [22]. While no direct studies have compared hydroxamates to phosphonates on TiO₂, there is evidence that hydroxamates may be more suitable anchors than carboxylates for water-oxidation photoanodes, especially given that hydroxamic acids are oxidation resistant, stable under neutral and basic aqueous conditions, and synthetically accessible directly from carboxylic acid functional groups, as shown in Fig. 4 [24].

Another useful anchoring group for the attachment of molecular species to TiO_2 is acetylacetonate, a 3-substituted-2,4-pentanedione (Fig. 2D) [25–27]. Mn^{II}–terpyridine complexes bound to TiO_2 via acetylacetonate anchors resisted detachment under aqueous conditions better than complexes bound via carboxylate anchors and showed efficient interfacial electron transfer



Fig. 4. Hydroxamic acids (where R=aryl) can be synthesized directly from carboxylic acids, as reported by Yavin et al. [24].

to TiO_2 upon visible-light excitation [25]. Acetylacetonate anchors have also been shown to adsorb boron-dipyrromethane (BOD-IPY) derivatives to TiO_2 [26]. Although the incorporation of an acetylacetonate functionality on photosensitizers and catalysts can be synthetically challenging, various synthetic routes have been developed for the construction of 3-substituted-2,4-pentanediones from aryl halides, as shown in Fig. 5 [28–31]. The acetylacetonate anchor is another promising choice for a photoanode that operates under aqueous and oxidative conditions.



Fig. 5. Synthesis of aryl-acetylacetonate from aryl halides via 3,5-dimethylisoxazole adduct (route A) [28,29] or via Cul/L-proline-catalyzed substitution with 2,4-pentanedione (route B) [30].



Fig. 6. Ruthenium–polypyridyl complex reported by Grätzel and coworkers, where X = Cl, Br, I, CN, or SCN.

Catechol functional groups are also known to bind bulk TiO₂ surfaces [32,33]. Catecholate has been established as a rigid aromatic anchor to bind Mn^{II} -terpyridine complexes to TiO₂ [33]. Photoexcitation of such complexes again led to rapid interfacial electron transfer to TiO₂. However the oxidizing power of the complex and further advancement of the oxidation state were limited by the relatively high electronic states of catechol allowing easy oxidation of catechol to the ortho-quinone [33].

A general systematic study that directly compares the stability and performance of each of the anchor groups to TiO_2 is still lacking in the literature. Such a study would be helpful for rational design of better photoanodes for light-driven water splitting.

2.2. Photosensitizers

An optimal dye for the sensitization of TiO_2 should strongly absorb photons across a wide range of wavelengths in the visible region, be photostable, and have suitable anchoring groups to bind to the semiconductor surface. In order for the thermodynamic driving force to be large enough for photocatalytic water oxidation, the reduction potential of the oxidized photosensitizer should be positive of the catalytic onset potential for water oxidation plus the overpotential required by the water-oxidation catalyst. Significant progress has been made in the development of a wide range of metal complexes [7,14], porphyrins [34], and organic dyes [35] for the sensitization of TiO₂.

2.2.1. Ruthenium-polypyridyl sensitizers

Because of their broad coverage and high molar absorptivity in the visible region and acceptable redox potentials, ruthenium-tris(bipyridyl) complexes are appealing photosensitizers for light-driven water-splitting photoanodes [36–38]. In general, ruthenium-polypyridyl complexes have broad absorption spectra, long-lived excited-state lifetimes, and good electrochemical stability. Spectroscopic and electrochemical properties can be tuned to optimize performance by substituting the ancillary ligands, typically bipyridines or terpyridines, with different functional groups.

Grätzel and coworkers reported a series of ruthenium complexes of the form $[Ru(4,4'-(COOH)_2 bpy)_2(X)_2]^{2+}$, where X = Cl, Br, I, CN, or SCN (Fig. 6), that proved to be excellent photosensitizers for TiO₂. In particular, the thiocyanato complex $(NBu_4)_2[Ru(4,4'-(COOH)(COO)bpy)_2(NCS)_2]$, also called N719 or "red dye", exhibited an extinction coefficient of ~14,000 M⁻¹ cm⁻¹ at 534 nm and an incident photon-to-current conversion efficiency (IPCE) exceeding 80% between 480 and 600 nm [39]. It has been suggested that thiocyanate ligands improve visible-light absorption and facilitate charge transfer between the photoexcited chromophore and



Fig. 7. A number of heteroleptic ruthenium sensitizers of the form $[Ru(4,4'-(COOH)_2bpy)(4,4'-(R)_2bpy)(NCS)_2]$ where R=alkyl thiophene [45,46], alkyl furan [46], phenylene vinylene [47,48], or 2-thiophene-2-yl-vinyl [49] exhibited high extinction coefficients.

the iodide/triiodide redox mediator, leading to higher DSSC efficiencies [40,41]. Both linkage isomers of the SCN⁻ complex are probably involved [42]. Attempts to extend absorbance to longer wavelengths resulted in the development of N749, or "black dye", a ruthenium complex with three thiocyanato ligands and a terpyridine ligand with three carboxylate anchors. N749 has a red-shifted MLCT band and a broad IPCE spectrum extending into the near-IR region up to 920 nm [43]. A ruthenium complex with two thiocyanato ligands and a quaterpyridine ligand with two carboxylate anchors and two *tert*-butyl substituents also exhibited a red-shifted absorption spectrum but had a lower IPCE, possibly due to aggregation of the sensitizer on TiO₂ [44].

Ruthenium complexes with higher extinction coefficients in the visible region were also explored in order to harvest incident light more efficiently. Higher extinction coefficients up to $24,200 M^{-1} cm^{-1}$ at 554 nm [45] were exhibited by a number of heteroleptic ruthenium sensitizers of the form [Ru(4,4'-(COOH)₂bpy)(4,4'-(R)₂bpy)(NCS)₂] where R included electron-rich substituents such as alkyl thiophene [45,46], alkyl furan [46], phenylene vinylene [47,48], or 2-thiophene-2-yl-vinyl, as shown in Fig. 7 [49].

2.2.2. Porphyrin sensitizers

Porphyrins have been widely studied as biomimetic light harvesters in artificial photosynthesis [50]. Porphyrin-based donor-acceptor dyads have been used to study the lifetime and charge recombination of photoinduced charge-separated states [51,52]. Porphyrins have also been used as chromophores to study photoinduced electron transfer to catalytic electron mediators via non-covalent interactions [53,54]. One advantage of porphyrins over ruthenium complexes as photosensitizers is that their absorption spectra generally extend further towards the near-IR region. Additionally, porphyrins often exhibit high molar extinction coefficients as well as reasonable IPCE in the visible region [10]. Porphyrin sensitizers have been used in DSSCs that achieve over 10% overall power conversion efficiency [12,55,56].

A potential problem with porphyrins as photosensitizers is that they have an inherent tendency to aggregate. Aggregation can lead to interactions between photoexcited species and ground-state species degrading their efficiency as photosensitizers. One solution is the introduction of coadsorbates on the surface, such as poly(4-vinyl-pyridine) (PVP) [57] or chenodeoxycholic acid [58] (Fig. 8). Another way to prevent aggregation is to incorporate bulky substituents, such as *tert*-butyl groups, on the peripheral *meso-* or β -positions of the porphyrin. However, making stepwise modifications can be challenging because tedious synthetic routes



Fig. 8. Coadsorbates used to prevent dye aggregation on the surface of titanium dioxide, including poly(4-vinyl-pyridine) (PVP) and chenodeoxycholic acid (CDCA).

are required, particularly for non-symmetric porphyrins. D'Souza and coworkers reported an alternative self-assembly approach for the immobilization of zinc porphyrins that lack explicit anchoring groups on TiO₂ via axial coordination of the metal center to a surface-adsorbed ligand [59]. Applying this approach, symmetric macrocycles can be used as chromophores, and the metal center or axially coordinated anchoring group may be varied to optimize photocurrent generation.

High-potential porphyrins have been proposed as suitable light harvesters for light-driven water splitting [60,61]. Electronwithdrawing pentafluorophenyl groups can be incorporated at the *meso*-carbon of a zinc porphyrin to induce an electron deficiency that leads to a positive shift in the ground-state reduction potential of the complex. Consequently, the holes remaining on a highpotential photooxidized porphyrin are thermodynamically capable of driving water oxidation.

2.2.3. Organic sensitizers

Hundreds of organic dyes have been synthesized as photosensitizers for metal oxide surfaces [10,35]. Metal-free organic dyes are viable alternatives to expensive ruthenium-based sensitizers and can exhibit very high molar extinction coefficients, even on the order of 100,000 M⁻¹ cm⁻¹ [62]. Their structures can be very diverse, but they often follow the general design principle of incorporating a donor group, a π -conjugated bridge, and an acceptor group (D- π -A). The acceptor group is anchored to the TiO₂ surface and should have good electronic overlap with the metal oxide conduction band to facilitate electron injection.

The classic D- π -A design, with A nearest the TiO₂ surface, is intended to promote a directional shift of the photoexcited state electron density from D to A and thus towards the semiconductor surface. Some of the best donor groups include electron-rich aryl amines, aminocoumarins, indolines, and N,N-dialkylanilines. The π -linker is designed to facilitate charge transport through the molecule. Frequently chosen π -conjugated linkers include thiophene units or phenylene vinylene units. The most common acceptor group in organic dyes is cyanoacrylic acid, which also acts as an anchor, because the LUMO overlaps with the bulk surface. Notable organic dyes in DSSCs include the indoline dyes reported by Ito et al. that give between 8.0% and 9.5% efficiency [63,64] and an aminocoumarin-bithiophene-cyanoacrylic acid dye known as NKX-2677 reported by Hara et al. to give up to 8.1% efficiency [65], as shown in Fig. 9. As in the case of porphyrins, the extended π aromatic systems of many organic dyes often lead to aggregation, which sometimes necessitates the use of coadsorbates for better performance.

Organic light harvesters have also been shown to advance the oxidation state of molecular water-oxidation catalysts. In one example, an organic linker consisting of a 4-phenyl-terpyridine ligand attached to a 3-phenyl-acetylacetonate via an amide bond absorbs visible light and transfers electrons to the conduction band of TiO_2 to photooxidize a Mn^{II} metal center [25]. This occurs despite its poor absorption in the visible region. Additionally,



Fig. 9. Organic dyes for DSSCs, including the coumarin dye NKX-2677 reported by Hara et al. and the indoline dye D205 reported by Ito et al.

this chromophoric linker can attach a high-valent oxomanganese water-oxidation catalyst covalently to TiO_2 and advance its oxidation state upon photoexcitation with visible light [66].

2.3. Immobilization of catalysts on a semiconductor surface

In a light-driven water-splitting photoanode, immobilization of the catalyst on the semiconductor surface facilitates closer proximity to light-harvesting sensitizers, thereby enabling more efficient electronic communication between the catalyst and the photooxidized chromophore. Immobilization of the catalyst may also prevent oxidation of one catalyst by a neighboring catalyst in a highly oxidized form that could lead to decomposition of the active catalyst.

2.3.1. Covalent attachment through surface-adsorbed sensitizer

In order to favor fast electron transfer, the metal catalyst center and the chromophore may be covalently linked. In essence, the chromophore becomes part of the ligand of the catalytic center and provides an anchoring group for covalent attachment of the catalyst–chromophore assembly. Both molecular and heterogeneous water-oxidation catalysts have been advanced with visible light using this binding architecture.

Photooxidation of a light-absorbing terpyridine linker immobilized on TiO₂ using either a hydroxamate, acetylacetonate, or catecholate anchor facilitates interfacial electron transfer to TiO₂ with subsequent oxidation of a Mn^{II} metal center [22,25,33]. When terpyridine was modified with a chromophoric amide linkage to an acetylacetonate anchoring group (L), the dimeric complex [Mn^{III/IV}₂(L)₂(μ -O)₂(OH₂)₂]³⁺ was assembled on TiO₂ [66]. This complex could be oxidized to the EPR-silent Mn^{IV/IV} form using visible light at cryogenic temperatures, although no oxygen production was observed upon illumination at room temperature.

Mallouk and coworkers demonstrated an overall water-splitting system where a ruthenium–tris(bipyridyl) complex served as both a chromophore and molecular bridge between a heterogeneous nanoparticulate catalyst and the metal oxide semiconductor surface [36]. Phosphonate anchors on one bipyridine ligand of the ruthenium complex were selective for attachment to the TiO₂ semiconductor surface while a malonate substituent on another bipyridine ligand was selective for coordination to the nanoparticulate $IrO_2 \cdot H_2O$ water-oxidation catalyst.

2.3.2. Suspension in a Nafion membrane

Another strategy for immobilizing a catalyst on an electrode surface is suspension in a polymeric network. The polymer should slow diffusion of the catalyst away from the sensitizer while allowing transport of protons and electrons between the catalyst and the electrode. In this case, the catalyst is not directly bound to the semiconductor surface but is instead trapped within the diffusion limit of the electrode. The most common polymer employed in the assembly of water-oxidation photoanodes is Nafion, a perfluorinated resin with acidic sulfonate head groups. Because of its perfluorinated backbone, Nafion is very oxidation resistant. Furthermore, Nafion is highly permeable to protons and other cationic species, which interact electrostatically with the deprotonated sulfonate head groups. Nafion is not itself conductive, but electrons can be transported through the membrane by redox interactions between neighboring redox-active species.

Nafion has been used in a few molecular systems as an alternative to covalent modification of the catalyst coordination environment. Recently, Li et al. demonstrated that a ruthenium catalyst, $[Ru^{III}(L)(4-picoline)_2]^+$ (L=4,4'-(COOH)_2bpy), could be doped into a Nafion membrane covering TiO₂ sensitized with $[Ru(bpy)_2(4,4'-(PO(OH)_2)_2bpy)]^{2+}$ [67]. The acidic pH of the Nafion membrane inhibited light-driven catalysis, but neutralization of the Nafion solution overcame this problem, as the onset potential for water oxidation is pH-dependent and favored at basic pH. Similarly, Brimblecombe et al. demonstrated that a manganese cubane complex, $[Mn_4O_4L_6]^+$ where $L = (MeOC_6H_4)_2PO_2^-$, suspended in a Nafion membrane on TiO₂ sensitized with a ruthenium-polypyridyl dye could oxidize water when illuminated with visible light [37]. However, the catalyst has been observed to be reduced to Mn^{II} and reoxidized to a catalytically active, heterogeneous manganese oxide within the Nafion layer [68,69].

Metal oxide catalysts have also been immobilized on metal oxide surfaces using Nafion. Pillai et al. reported the immobilization of RuO₂ nanoparticles and $[Ru(bpy)_3]^{2+}$ in Nafion on TiO₂ and observed light-driven oxygen evolution [70]. Increasing the thickness of the layer allowed the permeation of more $[Ru(bpy)_3]^{2+}$ and thus increased the observed photocurrent. Hara and Mallouk reported the deposition of colloidal IrO₂ particles and $[Ru(bpy)_3]^{2+}$ in Nafion on a conducting glass surface [71]. The polyanionic membrane stabilizes the colloidal particles in the same way that citrate or polyethylene glycol has been used in other preparations to prevent aggregation. In addition, the Nafion-stabilized particles outperform citrate-stabilized IrO₂ in both turnover frequency and total turnover number. Nafion is a suitable strategy for immobilization of either molecular or metal oxide catalysts.

2.3.3. Direct adsorption to metal oxide surface

In an alternative approach, the catalyst may be directly anchored to the semiconductor surface. This strategy has been employed for covalent attachment of the $[Mn^{III/IV}_2(tpy)_2(\mu-O)_2(OH_2)_2]^{3+}$ complex on TiO₂ surfaces, presumably through a bridging oxo-group between Mn^{IV} and a Ti^{IV} center on the particle [72]. This linkage changed the electronic structure of the Mn^{IV} center, evidenced by a difference in the hyperfine coupling constant in the EPR spectrum of the dimer. Similar behavior has also been observed for the complex $[(bpy)_2 Mn^{III}(\mu\text{-}O)_2 Mn^{IV}(bpy)_2]^{3+}$ adsorbed into the channels of Cr^{VI}-doped AIMCM-41 nanoporous silicon oxide [73]. Cr-doped AlMCM-41 is a photosensitizer for iridium-based water oxidation [74]. More recently, direct deposition has been employed in the design of a TiO₂ photoanode using a molecular iridium water-oxidation catalyst codeposited directly on TiO₂ with a highpotential perfluorinated porphyrin photosensitizer (Fig. 10) [60]. This design involved the introduction of an anchoring group onto an ancillary ligand of the catalyst; the anchoring group coordinated to the semiconductor surface while the catalyst open site was



Fig. 10. Codeposition of a high-potential porphyrin sensitizer and a molecular iridium water-oxidation catalyst on TiO₂ for a light-driven water-oxidation photoanode [60].

accessible to the solvent. Codeposition of the photosensitizer and catalyst was chosen because no photocurrent was observed when the catalyst and chromophore were directly linked prior to attachment to the surface via a carboxylate anchoring group on the porphyrin. One possible explanation for the absence of photocurrent is heavy-atom quenching of the photosensitizer excited state when the catalyst is linked to the porphyrin. Furthermore, the method of codeposition allows variation in the ratio of catalyst and photosensitizer, which may be helpful for the transfer of multiple electrons.

The dinuclear ruthenium catalyst $[Ru_2(\mu-bpp)(\mu-OAc)(t-tpy)_2]^{2+}$, where bpp=bis(2-pyridyl)pyrazolato anion and t-tpy=4-(*para*-pyrrolylmethylphenyl)-2,2':6',2"-terpyridine, has been linked to an FTO or vitreous carbon sponge (VCS) surface via electropolymerization of pendant pyrrole groups [75]. By tethering the catalyst to the surface, bimolecular deactivation pathways were suppressed and performance of the catalyst was improved. This system has not been incorporated into a photochemical device, but it does demonstrate how immobilization can be effective for improving catalytic efficiency.

3. Physical processes

Understanding the physical processes involved in systems for photocatalytic water oxidation is important for design and optimization. A summary of these processes is diagrammed in Fig. 11. First, photons are collected by the chromophore, triggering electron injection into the semiconductor. The hole remaining on the dye advances the oxidation state of a nearby catalyst, while the electrons travel through the semiconductor to an electrode where they are collected by redox species for fuel production. In the context of solar fuel production, this whole process can be divided into three distinct sub-processes: light harvesting, electron injection, and charge transport.

3.1. Light harvesting

A major limitation of the water-oxidation system described by Fujishima and Honda is that it requires UV illumination with wavelengths shorter than 385 nm to promote electrons across the 3.2 eVband gap of TiO₂ [6]. Some researchers have attempted to shift

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Fig. 11. A summary of the physical processes relevant to solar fuel production using molecular photoanodes. Blue arrows indicate the desired flow of electrons, and red arrows show deactivation processes.

the absorption into the visible region by developing non-oxide semiconductors [76], doping wide band gap semiconductors [77], adding secondary nanoparticles [78–80], or sensitizing the surface with dyes that absorb photons over the full range of the solar spectrum [34,39,55,81–85]. An important aspect within the context of DSSCs has been the use of nanoporous thin films with a large surface area for dye binding that allows for a large absorption cross section [8,86]. For the reasons discussed in Section 2.2, ruthenium-based polypyridyl complexes, porphyrins, and organic dyes have been chosen most often as the light-harvesting species for water-oxidation photoanodes [36–38,60]. Understanding the photophysics and light-harvesting mechanisms of these species is essential for improving the efficiency of photocatalytic cells.

3.1.1. Ruthenium–polypyridyl sensitizers

The UV-visible spectrum of ruthenium–polypyridyl complexes is dominated by a broad feature extending from 375 to 550 nm with a typical absorbance maximum around 450 nm. This feature corresponds to MLCT excitation from the *d* orbitals of the Ru²⁺ to the π^* orbitals of the conjugated bipyridine ligands [87]. The shoulder extending to longer wavelengths arises from MLCT states that are predominantly triplet in character.

As shown by transient absorption spectroscopy, relaxation from the ¹MLCT state to the ³MLCT state occurs within 100 fs after photoexcitation. This fast rate of intersystem crossing is ascribed to increased spin–orbit coupling due to the heavy-atom effect. The resulting ³MLCT state has a lifetime on the order of nanoseconds [88,89]. The heavy-atom effect is also responsible for altering the excited-state lifetimes of ruthenium–polypyridyl complexes bound to the metal oxide surfaces. For [Ru(bpy)₂(4,4'-(PO(OH)₂)₂ bpy)]²⁺ adsorbed to ZrO₂, the average lifetime of the MLCT excited state was found to decrease with increased dye loading due to quenching of the excited state by adjacent Ru^{II} centers [90].

3.1.2. Porphyrin sensitizers

The photophysical properties of porphyrins, metalloporphyrins and their excited states have been studied in great detail due to their importance in photosynthetic systems [87]. Porphyrins generally have two main spectroscopic features in the visible region that are assigned to electronic transitions. The Q-band results from excitations from the ground state to the first singlet excited state (S₁) and is typically observed between 500 and 600 nm. The Soret band, or B-band, is generally observed near 400 nm and arises from excitations from the ground state to the second singlet (S₂) state. Both of these transitions are π - π * transitions that involve the conjugated π systems of the porphyrin rings. Lifetimes of the S₂ state



Fig. 12. Energy level diagram showing the approximate reduction potentials of the excited states of some common classes of sensitizers and the conduction band edges of TiO_2 , ZnO, and SnO_2 and the timescales of recombination processes.

are typically less than 100 fs although some zinc porphyrins exhibit S₂ lifetimes of 1–2 ps [87,91–93]. The S₁ states are longer-lived with lifetimes on the nanosecond timescale [87,92]. When a heavy metal ion is incorporated into the porphyrin ring, the S₁ lifetime is decreased due to spin–orbit coupling, which leads to relaxation to a triplet state. Although these triplet states can have millisecond lifetimes, they are typically not positioned with suitable energy levels for interfacial electron injection (see Fig. 12). Energy level diagram showing the approximate reduction potentials of the excited states of some common classes of sensitizers and the conduction band edges of TiO₂, ZnO, and SnO₂ and the timescales of recombination processes.).

The π systems of the porphyrin rings can interact to form extended arrays when in close proximity. Aggregation of free-base porphyrins in solution has been shown to cause a 10-fold decrease in excited-state lifetimes due to the prevalence of triplet-triplet annihilation of the excited state [94]. Lu et al. observed that aggregation of a series of functionalized zinc porphyrins on TiO₂ nanoparticles increased the energy-transfer rate between molecules and decreased excited-state lifetimes [95].

3.1.3. Organic sensitizers

As discussed in Section 2.2.3, organic sensitizers have also been successful as chromophores in DSSCs due in part to their high molar extinction coefficients and broad visible absorption [35,84]. The primary optical transitions for organic dyes are typically π – π * transitions involving their conjugated π systems. Many organic dyes incorporate a donor-conjugated linker-acceptor (D– π -A) triad in order to facilitate electron injection. In a D– π -A dye, the highest occupied molecular orbital (HOMO) is centered on the donor, but the lowest unoccupied molecular orbital (LUMO) is primarily located on the acceptor, which is bound to the semiconductor surface. Excitation from the ground state to the excited state results in the transfer of charge from the donor to the acceptor and initiates electron movement towards the surface of the metal oxide.

3.1.4. Light harvesting and water oxidation

An outstanding challenge in the development of wateroxidation systems is optimization for efficient activation with visible light. In one example from Puntoriero and coworkers, a tetranuclear ruthenium–polypyridyl dendrimer was substituted for $[Ru(bpy)_3]^{2+}$ in a water-oxidation scheme described by Mallouk and coworkers [96–98]. This allowed water oxidation to occur at wavelengths up to 700 nm, where monomeric $[Ru(bpy)_3]^{2+}$ is ineffective. In the context of DSSCs, similar dendrimeric structures have been shown to increase light harvesting and cell efficiency [99]. Following this model, it is natural to expect that strategies that increase the efficiency of DSSCs should be valuable for improving the functionality of water-oxidation systems.

3.2. Electron injection

Once the adsorbed dye molecule has been photoexcited, a charge-separated state must be achieved via interfacial electron transfer from the dye excited state into the nanoparticle. The energy of the dye excited state relative to the conduction band edge of the semiconductor and the relative rates of electron injection and excited-state relaxation are two important considerations for the success of this process.

The relative energy levels for some of the most common semiconductors and dye molecules are presented in Fig. 12. While the energetics of TiO₂ and ZnO are fairly similar, the conduction band edge of SnO₂ lies at a more positive potential [100,101]. Electron injection into all three semiconductors is favorable for most ruthenium–polypyridyl dyes from both the ¹MLCT and ³MLCT states. The ground states of porphyrins tend to be more oxidizing, and electron injection into TiO₂ is typically only favorable from the S₂ and S₁ states. The lowest triplet excited states tend to be close to the TiO₂ conduction band edge, or even lower (more positive), making electron injection from those states much slower or even energetically forbidden.

A fast rate of interfacial electron transfer is important for efficient energy conversion. If the rates of the various deactivation processes in the molecule (see Section 3.1) are competitive with the electron injection transfer rate, the quantum yield of electrons can be significantly diminished. Many factors that influence the electron-transfer rates between weakly coupled redox species [102] are also expected to be important in interfacial electron transfer, including the requirement of isoenergetic donor and acceptor states with significant electronic coupling. Marcus theory was originally formulated to deal with systems with discrete energy levels and predicts electron-transfer rates limited by nuclear reorganization motion. In contrast, interfacial electron injection is often much faster than nuclear displacements and involves rates that are mainly determined by the electronic couplings H(E) and density of states $\rho(E)$ of levels in the conduction band isoenergetic with the donor state in the adsorbate molecule [78,88,103,104]. Therefore, the natural extension of Marcus theory to the rate of interfacial electron transfer is given by Eq. (2):

$$k_{ET} = \frac{2\pi}{h} \int_{-\infty}^{\infty} dE \rho(E) \left| \bar{H}(E) \right|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left[-\frac{(\lambda + \Delta G_0 - E)^2}{4\lambda k_b T} \right]$$
(2)

While the density of states $\rho(E)$ is specific to the semiconductor, the electronic coupling H(E), the energy difference between the dye excited state and the conduction band edge of the semiconductor ΔG_0 , and the excited-state energy E of the donor state in the dye are all largely dependent on the nature of the chromophore and covalent attachment to the surface. The reorganization energy λ and temperature T are environmental factors.

3.2.1. Dye parameters

The nature of the functional group that binds the dye to the semiconductor surface is important for electron transfer because it establishes the electronic coupling between the dye and semiconductor. Carboxylate anchors have appropriate coupling through bonds to the TiO₂ surface to allow electron injection on a femtosecond timescale [88,104,105]. While adequate for DSSCs, carboxylate anchors are generally unstable under aqueous conditions and, therefore, less suitable for water-oxidation systems; phosphonate anchors offer increased aqueous stability and stronger binding to the TiO₂ surface [106,107]. Additionally, acetylacetonate (acac) and hydroxamate anchors were recently developed for robust immobilization of catalysts on TiO₂ under aqueous and oxidative conditions. Terahertz spectroscopy and computational simulations show comparable timescales and efficiencies for electron injection for these anchors when compared to their carboxylate analogues [22,25,66].

Comparisons of the electron injection dynamics for carboxylate vs. phosphonate anchors highlight the importance of electronic coupling in rate determination. Studying perylene-based sensitizers, Willig and coworkers observed a faster electron injection rate for carboxylate anchors [107]. They attributed this difference to increased extension of the perylene donor orbital over the anchor group, which resulted in increased electronic coupling to the TiO₂ conduction band. Similarly, calculated electron injection rates from isonicotinic acid were predicted to be twice as fast as from 4-pyridyl phosphonic acid [18] since the LUMO of isonicotinic acid is more delocalized over the TiO2 surface, suggesting increased interfacial electronic coupling. She et al. also observed faster injection kinetics for carboxylate anchors capable of electronic coupling with a donor group [106]. When this coupling was disabled by the inclusion of a CH₂ spacer, electron injection was faster through the phosphonate anchor as predicted by binding strength comparisons.

In addition to the identity of the anchoring group, the binding mode of the dye molecule can also affect the electron injection rate and efficiency. When fitting the electron injection dynamics of dyes on TiO_2 and SnO_2 , several researchers have observed multi-exponential behavior that they attribute to a distribution of electron injection times [108–110]. Single molecule kinetic measurements suggest that this distribution is a result of surfacebinding inhomogeneities [111,112]. A weaker binding mode of a given anchor has been associated with decreased electronic coupling and, thus, decreased electron-transfer rates [113]. However, strong binding does not always give strong coupling, as in the case of phosphonate anchors.

Quantum dynamics simulations of electron injection from pyridine-4-phosphonic acid to TiO₂ predicted injection times of 80 fs when adsorbed in a monodentate binding mode and 26 fs in a binuclear bridging mode [114]. In the monodentate binding mode, the phosphonic acid is coordinated to a single surface Ti^{IV} ion via a single oxygen atom, whereas in the bridging mode, the phosphonic acid binds through two oxygen atoms to coordinate two different Ti^{IV} centers. However, DFT-B3LYP calculations of orbital energy broadening of the adsorbate projected density of states estimated injection rates of 35 fs for the monodentate binding mode and 32 fs for the bridging mode, indicating no dependence on binding mode for injection from pyridine-4-phosphonic acid [18].

Direct comparisons between simulated and experimental data on interfacial electron transfer rely on ensuring that the surface and attachment mode of the model anchor to the TiO_2 is realistic. Since attachment generally proceeds with time and sometimes by heating, some surface reconstruction might take place during sensitization. However, due to the heterogeneity of the nanoparticle surface, direct structural observations are difficult to procure. Jakubikova et al., compared the recombination kinetics of catechol on 6 nm particles of TiO_2 to intramolecular charge transfer in a model coordination complex, (NH₄)[Ti(catecholate)₃] [114]. It was found that excited-state decay was monophasic in the model complex and multiphasic for catechol on TiO_2 with a fast component similar to the model complex and multiple slower phases in the nanoparticle system. The fast component in the nanoparticle system was assigned to recombination from the titanium center nearest the sensitizer, and parallels were drawn between the chelating binding mode of catechol on the surface and in the model complex. More recently, Benedict and Coppens have prepared and structurally characterized polyoxotitanate nanocrystals with catechol and isonicotinic acid bound to 5-coordinate Ti atoms that project from the surface [115]. Because these materials have well-defined stoichiometry, single-crystal X-ray diffraction studies are available and reveal only chelate coordination of catechol or isonicotinic moieties to single titanium centers. The polyoxotitanates are suggested as models for TiO₂, and, thus, the valuable structural insights about binding modes may be applicable to larger TiO₂ nanoparticles as well.

The linking group, which connects the anchoring group to the remaining portions of the sensitizer, can also influence the electronic coupling and, thus, the rate of electron transfer. Several groups have observed that lengthening the linker decreases the rate of electron transfer [106,116,117]. Electronic coupling can be further decreased if the linker breaks conjugation between the anchor and the chromophore. Investigating a series of rhenium polypyridyl complexes bound to TiO₂, Asbury et al. observed that the rate of electron injection was 200 times greater in the absence of a CH₂ spacer [118]. Inserting two more --CH₂ spacers decreased the electron injection rate by an additional factor of 13.7. The addition of the first methylene spacer not only increases the overall length of the molecule but also breaks the conjugation essential for electronic communication whereas the addition of more --CH₂ spacers increases only the distance between the chromophore and the semiconductor surface [106,117].

Similarly, quantum dynamics simulations of electron injection from catechol on TiO₂ showed that the electronic structure of the photoexcited state can have a large effect on injection [119]. Injection from two catechol excited states was investigated. The first excited state, corresponding to electron photoexcitation into the catechol LUMO, lacked strong orbital overlap between the catechol adsorbate and the d orbitals of the coordinated Ti^{IV} . This poor overlap prevented through-bond injection, forcing the photoexcited electron to be coupled through space to a nearby surface Ti^{IV} ion. The computed injection time from this excited state was 6 fs. In the second excited state, corresponding to electron photoexcitation into the catechol LUMO + 1, the donor catechol adsorbate was strongly coupled to the Ti^{IV} d_{xz} orbital. The computed injection time for through-bond transfer was 3 fs, twice as fast as through space. The difference in injection times was not due to a difference in the conduction band density of states, as the excited states energies were nearly degenerate, but rather due to a difference in the strength of the electronic coupling as determined by the symmetry of donor and acceptor states. A similar dependence on the nature of the excited electronic state was observed in simulations of interfacial electron transfer from [Ru(tpy(PO(OH)₂))(tpy)]²⁺ to TiO₂ [114]. Excited states with a node in the electron density at the carbon atom of the pyridine ring bound to phosphorus resulted in a characteristic injection time of ~ 10 ps while excited states without a node in the same position had shorter injection times of ~ 1 ps.

3.2.2. Metal oxide parameters

The properties of the metal oxide can also influence the rate and efficiency of electron transfer. Although many metal oxides, including In_2O_3 , WO_3 , NiO, Nb_2O_5 and $BiVO_4$, have been investigated, TiO_2, SnO_2, and ZnO have been the most widely studied [120–125]. Using a variety of experimental methods and conditions, several groups have determined the ordering of electron injection rates as follows: TiO_2 > SnO_2 > ZnO [108,120,126,127]. The commonly accepted explanation for these relative rates is that a

higher density of states increases the electron injection rate [108]. TiO_2 has the highest density of states because its conduction band is composed primarily of empty *d* orbitals whereas the conduction bands of SnO_2 and ZnO are largely *sp* in character. SnO_2 has an advantage over ZnO because of its more positive band edge potential. The excited-state reduction potentials of many sensitizers lie close to the band edge of ZnO where the density of states is lower.

3.2.3. Environmental parameters

In a functioning water-oxidation solar cell, the sensitized thin film is surrounded by an aqueous environment. Solution properties, including pH and dielectric constant, influence electron injection. The pH of the solution surrounding the thin film is important because the TiO₂ conduction band becomes more positive upon reduction of the pH, increasing the free energy difference between the excited state of the adsorbate and the conduction band edge [109,128,129]. When compared to that of $Ru(4,4'-(COOH)_2 bpy)_2(NCS)_2$, the electron injection rate for (NBu₄)₂[Ru(4,4'-(COOH)(COO)bpy)₂(NCS)₂], also called N719, was found to be 30 times faster because the -COOH protons were coadsorbed on the TiO₂ surface during the sensitization process [109]. Rinsing the N719-sensitized film with neutral ethanol decreased the injection rate. The pH effect is found to be greater for TiO₂ than for SnO₂ [129]. Injection rates of [Re(4,4'-Q₂bpy)(CO)₃Cl], where Q is (-CH₂COOH) or (-CH₂PO(OH)₂), were measured as a function of pH on both TiO₂ and SnO₂. While the TiO₂ injection rate varied by three orders of magnitude over the range of pH 0-9, the rate varied by only a factor of 4 between pH 2–9 for SnO₂.

Temperature has also been shown to affect the rate of electron transfer. Using a nonadiabatic molecular dynamics simulation. Stier and Prezhdo reported electron-transfer rates for isonicotinic acid to rutile TiO₂ of 27.7 and 4.9 fs for 50 and 350 K, respectively [130,131]. The authors suggest that electron transfer may be divided into adiabatic and nonadiabatic contributions. In nonadiabatic electron transfer, the electron proceeds from the donor state to the acceptor state via a direct transition. This contribution is the result of weaker electronic coupling and may be described by rate equations such as Fermi's golden rule. By contrast, in adiabatic electron transfer a transition state must be crossed; this type is the result of stronger electronic coupling, and Marcus theory is more appropriate. Unlike adiabatic electron transfer, the nonadiabatic contributions are temperature dependent. At higher temperatures, fluctuations in the range of several tenths of an electron volt of the energy of the dye excited state allowed the dye to explore more of the conduction band and sample regions with a larger density of states.

In a similar example, mixed quantum-classical simulations have been used to model the influence of thermal motion on the electron injection from catechol into TiO_2 [132]. As discussed previously, the electronic structure of the catechol excited state influences the injection times at low temperature. However, when thermal motion is included, the injection rate increases since inhomogeneous broadening breaks the nodal symmetry of the excited states, mixing electronic states and, therefore, opening new injection pathways.

3.3. Electron transport

Once interfacial electron injection has occurred, the electron must percolate through the semiconductor thin film and reach the counter electrode before getting trapped or recombining with redox species in solution. Efficient charge separation thus requires the careful balance of a number of different processes including electron transport through the nanoparticle network as well as charge recombination between the electrons injected in the semiconductor and oxidized adsorbates on the surfaces or redox species in solution.

3.3.1. Electron transport within the semiconductor

Relative to electron transport in a bulk, single crystalline semiconductor, conductivity through nanoporous thin films is partially hindered by surface defects and contact junctions with disordered non-crystalline material between sintered nanoparticles. The bulk sheet mobility of TiO₂ is $56 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-2}$, whereas the mobility of nanoparticulate TiO₂ is $1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-2}$ [105]. Time-resolved THz spectroscopy measurements show that this decreased DC mobility is a result of the operation of different conductivity mechanisms [105]. While bulk TiO₂ displays Drude conductivity, nanoparticulate TiO₂ is better described by the Drude–Smith model.

The Drude model uses the kinetic molecular theory of gases to describe the electric conductivity in metals. The electrons are treated as a gas, which moves across immobile atomic nuclei. In the Drude model (Eq. (3)), the frequency-dependent complex conductivity $\tilde{\sigma}(\omega)$ is expressed in terms of the free-space permittivity ε_0 , the plasma frequency ω_p , angular frequency ω , and the carrier collision time τ , as follows:

$$\tilde{\sigma}_{\text{Drude}}(\omega) = \frac{\varepsilon_0 \omega_p^2 \tau}{1 - i\omega\tau} \tag{3}$$

Smith's correction to the Drude model is the addition of the c parameter, which accounts for the fraction of the carrier's initial velocity that is retained after a collision (Eq. (4)).

$$\tilde{\sigma}_{D-S}(\omega) = \tilde{\sigma}_{\text{Drude}} \left(1 + \frac{c}{1 - i\omega\tau} \right) \tag{4}$$

When c=0, the classical Drude model is retained. For TiO_2 nanoparticles, c is approximately -0.9, which suggests that the conductivity is dominated by backscattering at the grain boundaries between particles or by disorder-induced localization. Alternatively, the net conductivity in nanoparticles is limited because electrons cannot pass between particles as efficiently as they can move within them.

Connectivity between nanoparticles can be improved by sintering, which then increases conductivity of nanoparticulate films. For ZnO nanoparticles, annealed films were found to have a higher mobility $(232 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ vs. } 180 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ and a lower contribution from backscattering (c = -0.68 vs. c = -0.73) [133]. Even after sintering, the particles are surrounded by an amorphous shell, which is also the main component of the newly formed interparticulate junctions. Due to the conduction band offset between the crystalline and amorphous phases, potential barriers exist at the contact junctions between particles and electron transport is restricted (see Fig. 13) [134].

An atomistic model of the contact junction, formed upon annealing two 4 nm diameter TiO_2 nanoparticles, was obtained from molecular dynamics simulations [105]. A cylindrical sample extracted from the atomistic model revealed non-crystalline TiO_2 at the contact junction and nanoparticle extremities, as seen in Fig. 13. The core-shell structure of the nanoparticles was corroborated by XRD data showing a smaller crystalline nanoparticle diameter than determined by scanning electron microscopy.

The temperature-dependent dark DC conductivity data, shown in Fig. 13, for a thin film of TiO_2 nanoparticles have been properly described by a fluctuation-inducted tunneling conduction (FITC) model that accounts for the core-shell structure of the constituent thin-film nanoparticles [134]. The model revealed a thermally activated high-temperature regime above 250 K and a temperature-independent tunneling regime below 150 K. Parameters extracted from the FITC model gave an average tunneling junction barrier with a width of 3.45 nm, contact area of 71.6 nm², and a barrier height of 421 meV for a thin film composed of sintered Sigma–Aldrich TiO₂ nanoparticles. It was concluded that the tunneling barrier for electron conduction was the contact junction



Fig. 13. Plot of the dark DC conductivities of nanoporous TiO₂ films, made by sintering Sigma–Aldrich (filled circles) and Ishihara (open squares) nanoparticles. The solid lines are obtained using the fluctuation-induced tunneling conduction model. Inset: atomistic structure of two 4 nm particles sintered along with a cylindrical sample extracted from the particles showing the crystalline anatase core and non-crystalline shell.

Figure repro	oduced fi	rom 1	reference	[134]	with	permission.	Copyright	American
Chemical So	ciety 201	1.						

between nanoparticles due to the mobility band offset between the crystalline and amorphous phases.

The FITC model is consistent with more efficient charge transport within the nanoparticles than between them. This concept has also been pursued by several groups who predicted more effective charge transport through TiO_2 nanotubes and, therefore, better performance than nanoporous thin films in photoelectrochemical devices [135,136]. Experimental data, however, proved nanotubes to be no better than nanoparticles [137]. Unfortunately, electron transport in TiO_2 nanotubes is limited by a resonance due to exciton-like trap states [138]. For single-crystal rutile nanorods, however, Yang et al. have observed an increased electron diffusion coefficient compared to rutile nanoparticles [139].

3.3.2. Charge recombination

The recombination of electrons injected in the nanoparticles with holes left on the photooxidized adsorbates decreases the efficiency of charge transport and inhibits catalyst activation [140]. The recombination rate depends on several factors including electron transport in the host substrate and the nature of the sensitizer.

Durrant and coworkers have distinguished between recombination that is transport- or transfer-limited [141]. In the transport-limited case, recombination occurs from electrons that have become immobilized in trap states with energy below the semiconductor band edge. In order for the electrons and holes to combine, the electrons must hop from trap to trap until finding a dye cation. The distribution of shallow and deep trap states leads to non-exponential kinetics. Recombination from TiO₂ to Ru(4,4'-(COOH)₂bpy)₂(NCS)₂ (also known as N3) was found to be primarily transport-limited [142]. Similar observations have been made for zinc and free-base tetracarboxyphenyl porphyrins [143]. When compared to TiO₂, recombination from SnO₂ is approximately two orders of magnitude faster due to its lower density of trap states [144].

Transfer-limited recombination is observed when the physical separation between the dye cation and the metal oxide surface is increased [141]. Strategies to decrease recombination rates have mostly targeted the transfer-limited properties. In D- π -A organic



Fig. 14. The structures of the polyene-triphenylamine dyes studied by Albinsson et al.

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dyes, the donor becomes the cation and is kept far away from the semiconductor surface. Similar systems have included a built-in energy gradient making back electron transfer thermodynamically unfavorable [145].

Incorporating proton-coupled electron transfer (PCET) is also a promising strategy to decrease charge recombination rates [146] since it is often comprised of both transport- and transfer-limited components. Heimer et al. observed contributions from direct recombination (τ = 80 ns) and trap-state recombination (τ = 5 ns) for $Ru(4,4'-(COOH)_2 bpy)_2(NCS)_2$ and $Ru(5,5'-(COOH)_2 bpy)_2(NCS)_2$ [147]. In a related example, Albinsson and coworkers examined the injection and recombination dynamics of D5L2A1 and D5L2A3, two polyene-triphenylamine dyes with D- π -A structures (see Fig. 14) [148]. Calculations revealed that the LUMO was centered on the cyanoacrylic acid anchoring group of D5L2A1 but not on the rhodamine anchoring group of D5L2A3. Although both dyes exhibited similar electron injection kinetics, the rate of recombination to D5L2A3 was faster. Because the LUMO of D5L2A3 does not extend into the TiO₂ surface, electrons are injected to surface trap states and can recombine more readily.

3.4. Challenges to complete assembly

One of the biggest challenges facing the construction of a device for solar fuel production is optimizing the processes of light harvesting, electron injection, and charge transport while ensuring that the improvement of one process does not significantly interfere with the performance of the other two.

The relative time scales for electron injection and recombination are critical for cell performance, and the comparison of DSSCs made with TiO_2 and SnO_2 is a good example of how these essential processes can detrimentally compete with each other. Although SnO_2 has higher conductivity and electron mobility than TiO_2 , the resulting solar cells constructed from SnO_2 are usually less efficient than cells made with TiO_2 thin films [144]. Durrant and coworkers determined that both the higher electron diffusion constant and the positive shift in the conduction band edge relative to TiO_2 increase the recombination rate [144]. As a result, direct recombination competes strongly with dye regeneration and the device performance is degraded.

Another important aspect is the interplay between photoabsorption and electron injection efficiency and its impact on the overall cell performance. In photocatalytic cells for water splitting based on the coadsorption of an iridium catalyst and a perfluorinated porphyrin photosensitizer on TiO_2 thin films, coadsorption gave an increased photocurrent when illuminated with visible light, but the electron injection yield was lower than for the porphyrin sensitizer or catalyst alone [60]. Although the origin of this effect is presently unknown, these results suggest that the coadsorption of the sensitizer and catalyst is somehow altering and inhibiting the electron injection process.

In another system, Meyer and coworkers compared the electron injection dynamics of the $[(4,4'-(COOH)_2bpy)_2Ru(bpy-Mebim_2py) Ru(bpy)(OH_2)]^{4+}$ dimer to $[Ru(bpy)_2(4,4'-(PO(OH)_2)_2bpy)]^{2+}$ bound to the TiO₂ surface. By using the dimer instead of a monomer,

the time constant for back electron transfer was increased from 0.5 to $30 \,\mu s$. The electron injection efficiency, however, was 10 times lower for the dimer than the monomer [149].

4. Catalysis for light-driven water oxidation

The final consideration in the development of a molecular system for light-driven water oxidation is the choice of water-oxidation catalyst. The ideal catalyst would be robust and long-lived, operate at low overpotential (i.e., near the thermodynamic potential for water oxidation) and employ only earth-abundant materials. While no currently known catalyst meets these high expectations, much progress has been made in the development of fundamental understanding of water-oxidation catalysis in general. In the design of molecular systems for photoanodes, previously reported coordination complex or metal oxide water-oxidation catalysts have been adapted to interface with light-harvesting and electron-transfer components. Numerous water-oxidation catalysts based on various transition metals including manganese, cobalt, ruthenium, and iridium can be driven by chemical oxidants or by applied potential and have been reviewed elsewhere [150-152].

The catalyst is the heart of a water-oxidation photoanode. It is responsible for synchronizing the transfer of four electrons and four protons with the formation of an O–O bond to produce dioxygen from two water molecules. While the mechanism of water oxidation in photosystem II remains an area of much study, there are essentially two mechanisms for oxygen-oxygen bond formation in synthetic systems [153]. In the predominant model, a high-valent metal-oxo (M=O) or metal-oxyl (M-O[•]) species is generated by successive oxidation and deprotonation of a bound water molecule [4]. This electrophilic oxygen atom is attacked by a nucleophilic water molecule to form an O-O bond. After two more oxidation and deprotonation steps, O₂ is released. An alternative mechanism involves the interaction of two metal-oxo or metal-oxyl units [153]. The M–O units may be terminal or bridging, but in either case, they couple together to form an O-O bond, and O_2 is released in a step resembling reductive elimination.

In a light-driven system, the catalytic cycle is advanced through four successive oxidations by the oxidized photosensitizer. Consequently, all catalyst intermediates must be energetically accessible at the potential of the photosensitizer. The catalytic intermediates must also be stable on the timescale of electron transfer between the sensitizer and catalyst to avoid the release of partially oxidized products such as hydrogen peroxide or superoxide. Light-driven systems are in many ways analogous to those advanced by chemical oxidants. However, some extra consideration is required to match the lifetime and potential of the oxidized photosensitizer with the requirements of the catalyst.

4.1. One-photon, one-electron oxidation steps

Suitable catalysts for light-driven water oxidation must be advanced in one-electron steps. Because the catalysts chosen for study in light-driven systems are often studied in diffusional systems with chemical oxidants before application to the development of photoanodes, selecting known catalysts that can be powered by one-electron chemical oxidants such as Ce^{4+} or $[Ru(bpy)_3]^{3+}$ or by an electrochemical potential are possible contenders. Those catalysts that work exclusively with oxo-donor oxidants such as hypochlorite, oxone, or peroxides are less promising candidates.

4.1.1. Solution-phase oxidation with $[Ru(bpy)_3]^{2+}$ and a sacrificial electron acceptor

The simplest method for light-induced water oxidation is the use of photogenerated $[Ru(bpy)_3]^{3+}$ or a similar ruthenium– polypyridyl derivative in a diffusional solution system with a sacrificial electron acceptor. This approach requires no covalent modification of previously reported molecular water-oxidation catalysts. $[Ru(bpy)_3]^{3+}$ is a potent one-electron oxidant with a potential of +1.26 V vs. NHE, sufficient for the oxidation of water [154].

Several molecular water-oxidation catalysts have been reported to oxidize water with light-generated $[Ru(bpy)_3]^{3+}$ and a sacrificial electron acceptor like persulfate $(S_2O_8^{2-})$ or, less frequently, $[Co^{III}(NH_3)_5Cl]^{2+}$. Most of these catalysts are mononuclear or dinuclear ruthenium complexes [155-161]. As an alternative to traditional coordination compounds that contain labile or oxidizable organic ligands, Hill and coworkers have reported two polyoxometalate complexes that exhibit homogenous, light-driven water oxidation using $[Ru(bpy)_3]^{2+}$ and persulfate [162,163]. More recent work by Stracke and Finke [164] suggests that Hill's cobaltcontaining polyoxometalate is converted under electrochemical oxidation to the active catalyst, a heterogeneous cobalt oxide similar to that studied by Kanan and Nocera [185].

The combination of $[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$ as a solutionphase oxidant system has also been used to drive water oxidation on manganese, cobalt, ruthenium, and iridium oxide nanoparticles [165–169]. Notably, the choice of electron acceptor in these solution-phase systems is often $S_2O_8^-$, which can form sulfate radicals that have higher potentials (>3.45 V vs. NHE) than the oxidized $[Ru(bpy)_3]^{3+}$ and that may cause side reactions [170]. The mechanism for photogeneration of $[Ru(bpy)_3]^{3+}$ is shown in Eq. (5a–c).

$$[Ru(bpy)_3]^{2+} + h\nu \to [Ru(bpy)_3]^{2+*}$$
(5a)

$$[Ru(bpy)_3]^{2+*} + S_2O_8^{2-} \rightarrow [Ru(bpy)_3]^{3+} + SO_4^{\bullet-} + SO_4^{2-}$$
(5b)

$$[Ru(bpy)_{3}]^{2+} + SO_{4}^{\bullet-} \rightarrow [Ru(bpy)_{3}]^{3+} + SO_{4}^{2-}$$
(5c)

Karlsson et al. recently reported a Mn^{III}/Mn^{III} catalyst, shown in Fig. 15, that oxidizes water in the presence of either photogenerated $[Ru(bpy)_3]^{3+}$ and persulfate or by direct addition of $[Ru(bpy)_3]^{3+}$ generated from chemical oxidation of $[Ru(bpy)_3]^{2+}$ [171]. Comparing the results of both preparations of $[Ru(bpy)_3]^{3+}$ demonstrates that ruthenium and not sulfate radical is the oxidant responsible for water oxidation. This is the first manganese coordination complex reported to catalyze water oxidation for multiple turnovers with a one-electron oxidant.

Studies of solution-phase systems form the foundation for the development of chromophore-catalyst systems immobilized on



Fig. 15. This $Mn^{III/III}$ dimer oxidizes water in the presence of $[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$ under visible-light illumination [171].

an electron-accepting surface. Catalysts that work effectively with $[Ru(bpy)_3]^{3+}$ in solution are not guaranteed to be as effective when immobilized on TiO₂. In the solution-phase systems, the electron transfer from the excited ruthenium complex to $S_2O_8^{2-}$ is irreversible. Consequently, electron transfer from the sensitizer to the catalyst is the kinetically relevant step because recombination is insignificant. As a result, the time scale for electron transfer to the catalyst is limited by the lifetime of $[Ru(bpy)_3]^{3+}$ in solution, while in surface-bound systems, recombination of the electron in the semiconductor conduction band is often competitive with or faster than electron transfer from catalyst to chromophore.

4.1.2. Chromophore-catalyst dyads

Direct association of a chromophore and a catalyst may improve efficiency of electron transfer from the catalyst to the oxidized chromophore compared to a two-component solutionphase system. Several chromophore-catalyst dyads have been assembled by covalent modification of the ligand environment of previously reported manganese- or ruthenium-based water-oxidation catalysts. Aukauloo and coworkers applied this strategy by modifying the terpyridine ligands of the previously reported $[Mn^{III/IV}_2(tpy)_2(\mu-O)_2(OH_2)]^{3+}$ dimer and incorporating a ruthenium-polypyridyl dye through a 1,10-phenanthroline-4,5dione linkage to the ruthenium center, shown in Fig. 16 [172,173]. The modified terpyridine ligand was used to assemble a mixedvalence manganese dimer similar to that used for water oxidation with chemical oxidants, and one-electron transfer to form the Mn^{IV/IV} complex was observed. No noticeable shifts in the reduction potential of either manganese or ruthenium centers were observed, indicating that the modification to the ligand environment does not significantly affect the electronic structure of the catalyst or dye. Aukauloo and coworkers also report analogous intramolecular charge-transfer behavior with a Mn^{III}-salen complex with the salen ligand modified in a similar way [174].

In a comparable approach, the groups of Åkermark, Hammarström, and Styring have studied a dinuclear manganese system based on the bpmp (bpmp=2,6-bis[[N,N-di(2pyridylmethyl)amino]methyl]-4-methylphenol) ligand with a ruthenium–polypyridyl sensitizer linked through covalent modification of the 4-positions on polypyridyl and phenolate ligands [175,176]. The manganese dimer, shown in Fig. 17, can be oxidized from Mn^{III}/Mn^{III} to Mn^{III}/Mn^{IV}, demonstrating that advancement



Fig. 16. Mn^{III/IV} dimer linked to two ruthenium chromophores. This complex is observed to undergo reversible one-electron oxidation with visible-light illumination [172].



Fig. 17. Structure of a Mn^{II,II} dimer linked to a ruthenium chromophore though an amide linkage [176].

of the oxidation state is possible, even if catalytic turnover is not. An analogous dimeric ruthenium complex may also be photooxidized from Ru^{II}/Ru^{II} to Ru^{III}/Ru^{III} [177]. However, the excited-state lifetime of the ruthenium chromophore is less than 100 ps, which is attributed to heavy-atom quenching by the nearby ruthenium centers in the catalyst.

These systems demonstrate that photooxidation of a chromophore–catalyst dyad is possible. However, none of these systems have been observed to oxidize water by using visible–light

illumination owing to the difficulties of multiple light-driven electron transfers. Other multi-electron processes including reduction of CO₂ to CO [178,179], reduction of protons to H₂ [54], and reduction of O₂ to H₂O [180,181] have been accomplished by covalently linked chromophore–catalyst dyads.

4.2. Multiple-electron transfer

Because water oxidation is a four-electron process, a combined chromophore–catalyst system must be capable of transferring four electrons during the catalytic cycle. Successive oxidations are increasingly energetically demanding. However, most chromophores are suited only to one-electron cycling at a fixed potential, so each oxidation step of the catalyst must occur at a potential no higher than that of the chromophore. PCET can level the oxidation potentials of each successive intermediate by compensating for the increased positive charge through deprotonation of a coordinated water molecule. Furthermore, turnover requires the transfer of four electrons before O_2 is released, so catalytic intermediates must live long enough for four successive electron transfers to the photosensitizer to occur without dissociation of partially oxidized products to avoid degradation of the catalytic system by reaction of highly oxidizing intermediates.

Multiple-electron transfer is one of the most difficult hurdles in light-driven water oxidation, especially in manganese-based systems. There are several examples in the literature of attempts to interface the previously reported $[Mn^{III/IV}_2(tpy)_2(\mu-O)_2(OH_2)]^{3+}$ dimer to chromophores for light-driven water oxidation [66,73,172,173]. In each case, the one-electron oxidation from Mn^{III}/Mn^{IV} to Mn^{IV}/Mn^{IV} may be observed by EPR, but no further oxidation or production of oxygen has been reported. This may be due to the high potential of the Mn^{IV}/Mn^V couple. In another case of a Mn^{IV} center coordinated to three phenolate ligands connected by a 1,4,7-triazacyclononane (tacn) ring (Fig. 18), photochemical oxidation produces an oxidized phenolate ligand rather than a Mn^V complex, indicating that reaching the



Fig. 18. Mn^{II} complex linked to three Ru^{II}(bpy)₃ centers. With visible-light illumination, this complex undergoes two Mn-centered oxidations and one ligand centered oxidation [182].



Fig. 19. Schematic diagrams of four water-oxidation photoanodes that incorporate a catalyst and molecular chromophore on TiO₂. Oxygen detection has been reported for the systems shown in A, B, and D. Figures A and B reprinted with permission from references [36] and [37], respectively. Copyright 2009–2010 American Chemical Society. Figure D is from reference [38] – reproduced by permission of the Royal Society of Chemistry.

high oxidation states of a metal center is difficult without PCET [182].

Meyer and coworkers reported a system in which a TiO_2 or *nano*ITO surface is functionalized with a ruthenium–polypyridyl chromophore linked through a carboxylate anchor. The chromophore is then covalently linked to the $[Ru(Mebim_2py)(bpy)(OH_2)]^{2+}$ catalyst [149]. They report the photochemistry of this reaction in a propylene carbonate/water mixture, used to prevent dissociation of the carboxylate groups from the semiconductor surface. Spectroelectrochemical experiments demonstrate sequential oxidations of the ruthenium center of the catalyst, but injection into the TiO_2 conduction band is slow. Measurement of oxygen produced has not yet been reported for the TiO_2 -bound molecular assembly, but catalytic current was seen for the $[Ru(Mebim_2py)(4,4'-(CH_2PO(OH)_2)_2(bpy))(OH_2)]^{2+}$ catalyst without the chromophore on a *nano*ITO surface [183].

To date, the best solution to the difficulty of multiple-electron transfer has been the use of metal oxide catalysts. Metal oxide particles possess many active sites and are, thus, able to store multiple oxidizing equivalents and channel them together at one site to produce dioxygen from water [184]. Both precious and base metal oxides are known to oxidize water with $[Ru(bpy)_3]^{2+}$ and persulfate in solution-phase systems (Section 4.1.1). Additionally, one example of a small IrO_2 nanoparticle coordinated

to a ruthenium-polypyridyl sensitizer on TiO₂ has demonstrated oxygen evolution with illumination (Section 5) [36]. Cobalt oxide materials are known to catalyze water oxidation. Kanan and Nocera observed that incorporation of phosphate into cobalt oxide makes a more active electrocatalyst [185]. Recently, this catalyst has been deposited on ITO and interfaced with a NiMoZn proton reduction catalyst on a triple-junction amorphous silicon solar cell to do overall water splitting with solar-to-fuels efficiency of 2.5-4.7%, depending on the configuration [186-188]. The use of a silicon solar cell to power water oxidation and reduction with light is an alternative strategy to the use of molecular photosensitizers and semiconducting oxides. At present, the efficiency of this "artificial leaf" is largely limited not by the catalysts but by the solar cell. The cobalt-phosphate catalyst has also been deposited on hematite (Fe₂O₃) [189] and WO₃ [190] for light-driven water oxidation. However, more recent studies demonstrate that on hematite, cobalt is not acting as a catalyst, but rather enhances activity by reducing recombination [191].

5. Complete systems

The grand challenge in the development of light-driven water oxidation for solar fuels production is the coordination of molecular components that harvest visible-light energy and transfer electrons to advance a catalytic process. Only a handful of systems, shown in Fig. 19, are known to incorporate all three components—metal oxide semiconductor, molecular photosensitizer, and catalyst—in a complete system.

There are two measures of efficiency in a water-oxidation photoanode. The first is quantum efficiency, Φ , or the percent conversion of photons into charge separations (electron-hole pairs). The reported quantum efficiency of the Fujishima and Honda system is a modest 10%, leaving much opportunity for improvement [6].

The second measure is Faradaic or coulombic efficiency, which is the percent conversion of four electron-hole pairs into oxygen molecules. Calculation of Faradaic efficiency depends on an accurate method for quantification of oxygen produced by water oxidation. The most common technique is a Clark electrode, which measures the change in solution oxygen concentration. However, headspace detection methods including gas chromatography–mass spectrometry (GC–MS) and fiber-optic oxygen probes have also been used. Unambiguous detection of oxygen is the ultimate performance indicator for water-oxidation photoanodes. Current alone is not a sufficient indication of catalytic activity, since almost all possible impurities in a system are more easily oxidized than water and could provide an alternative electron source [192].

The first example of a functional system for visible-light-driven water oxidation with molecular components was developed by Mallouk and coworkers [36]. In this system, shown in Fig. 19A, a nanoparticulate anatase TiO_2 surface is sensitized with a heteroleptic ruthenium–polypyridyl chromophore bound through a phosphonate anchor. An IrO_2 nanoparticle catalyst is bound to ruthenium chromophore through a malonate linkage. The system produces oxygen when illuminated with visible light under a small bias voltage. However, the quantum yield is reported at 0.9%, and coulombic efficiency of oxygen production is roughly 20%. The relatively poor performance of this system is attributed to much faster recombination of electrons from the TiO_2 conduction band and the oxidized dye than electron transfer from the iridium catalyst to the oxidized dye.

Spiccia and coworkers describe a complementary system in which a TiO₂ layer on FTO is sensitized with a ruthenium-polypyridyl dye and coated with Nafion perfluorinated polymer doped with $[Mn_4O_4L_6]$ where $L = (MeOPh)_2PO_2^{-1}$ (Fig. 19B) [37]. When illuminated with visible light without an external bias voltage, the system oxidizes water with 90% coulombic efficiency. The much improved efficiency compared to the Mallouk system may be attributed to longer-lived charge separation between the oxidized dye and the TiO₂ conduction band in part because a carboxylate anchor was used rather than a phosphonate anchor as in the Mallouk system. Alternatively, the rate of electron transfer from the catalyst to the oxidized dye may be faster, thus competing against recombination of the dye and conduction band. The first-row transition metal catalyst may also participate by minimizing heavy-atom quenching of the dye excited state vs. the third-row IrO2 particle, leading to greater peak incident photon to electron conversion efficiency (IPCE). More recent studies have shown that the manganese cubane complex is not the active species for catalysis [68]. Instead, the complex forms a heterogeneous mixed-valent manganese oxide similar to birnessite. While the manganese oxide material is clearly catalytically active, this metal oxide-based system does not lend itself to catalyst optimization by molecular design.

Sun and coworkers developed a ruthenium analog to the Spiccia system by incorporating a $[Ru(6,6'-(COO)_2bpy)(4-picoline)_2]^+$ catalyst into a Nafion film, which is then cast onto TiO₂ sensitized with $[Ru(bpy)_2(4,4'-(PO(OH)_2)_2bpy)]^{2+}$ [38]. The system, shown in Fig. 19D, produced oxygen in the presence of visible light but only when the Nafion had been treated to raise the pH to 7.0 or higher. No information about quantum or Faradaic efficiency has been reported to date, but the catalyst has been observed produce 16 turnovers at a rate of 27 turnovers per hour.

A final example of a molecular assembly for light-driven water oxidation is the coupling of a molecular iridium catalyst with a high-potential porphyrin-based dye on TiO_2 (Fig. 19C) [60]. Both the perfluorinated porphyrin and the previously reported Cp*-Ir catalyst are functionalized with carboxylate anchor groups and codeposited on TiO_2 rather than covalently linked as in other systems. With a 0.3 V bias voltage, the combined system is reported to give significantly higher photocurrent, attributed to water oxidation, than any of the components separately. However, oxygen production has not yet been reported, so no full characterization is available for comparison.

6. Conclusions

The systems reviewed here represent the most recent advances in the design, synthesis, and characterization of photoanodes for light-driven water oxidation as a component of solar fuel production. The three parts of the photoanode—semiconductor, chromophore, and catalyst—have each been developed individually, yet few functional photoanodes exist. The greatest challenge to future work is the assembly of the pieces, especially the coordination of the photosensitizer and catalyst to transfer four oxidizing equivalents to release dioxygen and regenerate the catalyst resting state.

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