**Electron Transfer Dynamics in Fuel Producing Photosystems**

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**Abstract**

An often overlooked aspect of solar fuel production is the inherent mismatch between bulk charge carrier lifetimes and rates of charge transfer reactions. Considering water oxidation, interfacial charge transfer occurs on the millisecond to second timescales while bulk charge carrier lifetimes of metal oxides are typically in the fast picosecond – nanosecond regime. For charge transfer to efficiently compete with charge recombination, strategies that substantially increase the charge carrier lifetime need to be applied. In this chapter, we discuss the magnitude of the kinetic mismatch, overview common effective charge separation strategies that address this mismatch and highlight recent developments in our understanding of these processes. We also touch upon recent advances in determining the chemical nature of key reaction intermediates.

**Keywords**

Charge carrier dynamics, kinetic competition, recombination, transient absorption spectroscopy, internal electric field, cocatalyst

**Kinetic Competitions vs Recombination**

Increased concern regarding our current CO2 emission trends has led to significant research efforts in harnessing the most abundant renewable energy source, solar power.[1] The conversion of solar energy into chemical bonds has become an attractive strategy to produce combustible fuels, termed solar fuels, in a carbon-neutral manner.[2] This strategy addresses solar intermittency issues by decoupling energy production and energy consumption, and the formation of chemical bonds simplifies storage and transport. Inorganic semiconductors have shown the most promise for solar fuels production. From the point of view of the light-absorbing semiconductor, charge balanced chemical reactions involving electron transfer (reduction reaction) or hole transfer (oxidation reaction) take place at the semiconductor-liquid interface. On the one hand, chemical reduction produces the solar fuel, most commonly proton reduction to produce hydrogen,[3] or CO2 reduction to yield CO, methane, or methanol, amongst other possible products.[4] On the other hand, a chemical oxidation process takes place. A sustainable target is water oxidation, although it has been identified that the timescale of this half reaction on metal oxides is typically on the order of 10 ms – 1 s[5-9] and often limits the overall efficiency of solar fuel production. In order to attain high efficiencies, photocatalysts typically overcome slow water oxidation kinetics either with an applied bias (by potentiostatic control or with a tandem photovoltaic cell)[10, 11] to slow down charge recombination or by using sacrificial electron donors, such as triethanolamine or Na2S–Na2SO3, with faster oxidation kinetics.[12, 13] Unless electron donors with suitable kinetics that produce large quantities of desirable value-added oxidation products, termed solar chemicals, are found, the use of sacrificial electron donors is bound to be unsustainable. One potential avenue is the oxidation of chloride in brine to form the value added products chlorine/hypochlorate.[14] Understanding the charge carrier dynamics in fuel producing photosystems is thus crucial to solve the general kinetic challenge of fast charge recombination outcompeting slow water oxidation (or in some cases slow proton/CO2 reduction).

Akin to photovoltaic cells, the main energy loss pathway for solar fuels systems is unwanted recombination of photogenerated electrons and holes. Any steps subsequent to photogeneration of charges will be in kinetic competition with recombination, and these competitions ultimately dictate device performance.[15] Solar energy conversion efficiencies over 20% are obtainable for multiple types of photovoltaic cells, including Si, GaAs, CdTe, and recently perovskites,[16] while there are limited number of examples of water splitting photosystems surpassing 10% solar-to-fuel conversion efficiencies.[11, 17] One may turn to the significant differences in charge extraction kinetics in both types of systems to explain the typically higher efficiencies of solar to electricity conversion. Transient electrochemical and optical spectroscopies, such as transient photovoltage or transient absorption spectroscopies, as well as frequency domains techniques, can provide detailed information regarding the charge carrier dynamics in solar energy conversion systems. With the aid of these techniques, the charge collection time needed for charges to reach the contact electrodes and be extracted from the system in photovoltaics cells have been determined to be typically on the timescales of ns-μs.[18, 19] However, for solar fuel systems, charges not only need to reach the semiconductor-electrolyte interface, but interfacial charge transfer must also occur to extract the charges. The timescales of interfacial charge transfers are typically a few hundreds of microseconds to milliseconds for proton reduction,[20, 21] and usually longer at 10 ms – 1 s for water oxidation. [5-9] Comparing these reaction kinetics to the timescale of charge recombination gives important insight (Figure 1). While there is a lack of data concerning charge carrier lifetimes under relevant operating conditions for many different types of novel photocatalysts, the bulk charge carrier lifetimes of metal oxides, such as TiO2,[22] hematite,[22] BiVO4,[23] range from ps to ns.[24] It might be a surprise that solar fuel producing systems may function at all when we consider that there may be up to a staggering 12 orders of magnitude mismatch in the lifetimes of the productive (i.e. interfacial charge transfer) and energy loss steps (i.e. charge recombination). Strategies are thus required to increase the charge carrier lifetime to ensure favourable kinetic competition of charge transfer reactions.

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Figure 1. A) Schematic representation of the timescales and competition between recombination and charge extraction from a semiconductor for photovoltaic and photocatalytic systems. B) Typical recombination pathways and timescales. W is the width of the space charge layer.

**Bulk vs Surface Kinetic Competitions**

Initial formation of an electron-hole pair leaves the charges near one another. Recombination of these charges occurs on a fast timescale (ps – ns) unless these charges are spatially separated. Different materials can show vastly different bulk recombination kinetics. For example, recombination in hematite has been measured to take place in 3 ps while the same process measured in TiO2 under similar conditions occurs in 6 ns, three orders of magnitude slower.[22] This may reflect the localised Fe-centred d-d nature of the optical transition in hematite compared to the spatially separated charge transfer character of TiO2 transition where the VB and CB are mainly composed of O 2p and Ti 3d orbitals, respectively.[25] Further charge separation is typically driven by energetic considerations. For example, charge trapping to lower energy sites may lead to spatial electron-hole separation and slow down charge recombination into the microsecond timescale.[23, 26] This charge trapping, however, also reduces charge carrier energetics and mobility. The kinetic competition between charge separation and bulk recombination determines how many charges may eventually reach the semiconductor/electrolyte interface and be available for interfacial charge transfer.[27]

When a semiconductor is placed in contact with an electrolyte, Fermi level equilibration induces ‘band bending’ of the CB and VB. An electric field is created for a region near the interface, called the space charge layer (SCL), or depletion region. For n-type semiconductors, upward band bending drives holes toward the electrolyte and electrons within the bulk, resulting in low electron density near the interface. A major consequence is the significantly increased lifetime of holes within the SCL vs the bulk. In the SCL, hole lifetime will be limited by surface or ‘back electron-hole recombination’ where bulk electrons need to overcome a significant energetic barrier to recombine with these surface holes, resulting in significantly slower recombination than bulk recombination (Figure 1B).[27] For example, electrochemical control of the Fermi level of hematite photoanodes has been used to control the extent of band bending and the width of the SCL.[22, 28] In the bulk, the lifetime of photogenerated charges saw modest lengthening from 6 ps to 200 ps under positive applied potentials. More significant were the changes observed on the microsecond – second timescales. A population of long-lived holes with lifetimes > 10 ms could only be observed at positive applied biases, and is correlated to the observed activity of the photoanode.[29, 30] The lifetime of the holes was effectively lengthened from picoseconds to the second timescale by hole transfer to the SCL where surface back electron-hole recombination is significantly retarded. As a result, water oxidation is able kinetically compete with surface recombination leading to photoactivity. Kinetic competition between surface recombination and charge transfer reaction determines how many surface charges participate in interfacial reactions.

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Figure 2. TAS decays of α-Fe2O3 showing the effect of applied bias and overlayers (‘cocatalyst’ CoOx or passivating Ga2O3) which reduce recombination. Decay of the long-lived (> 10 ms) signal is independent of sample composition and is attributed to water oxidation by hole accumulated on the surface. Reproduced from [28].

**Improving Kinetic Competitions**

To improve the yield of charge transfer reactions, one needs to either slow down detrimental charge recombination or increase the rate of productive charge transfer. Increasing the rate of charge transfer might be possible by adding a cocatalyst with advantageous catalytic properties compared to the light absorber.[31] Photogenerated charges in the light absorber would transfer to an appropriate cocatalyst, and finally reach a reaction partner in solution in a charge transfer step with lower activation energy. However, many studies of the role of cocatalyst layers in photoelectrodes have shown that cocatalyst addition increases the lifetime of charge carriers by enhancing charge separation or supressing recombination, rather than improving charge transfer kinetics (Figure 2).[8, 28, 32] In a striking example, it was shown for the case of BiVO4 with a CoPi cocatalyst that the major water oxidation pathway does not even involve the cocatalyst and hole transfer to water primarily originates from the BiVO4 layer.[33] The origin of the improved charge separation has been suggested to be caused by an internal electric field generated by the formation of a Schottky-type heterojunction between the light absorber and cocatalyst.

The generation of an internal electric field has indeed proved to be a general method to increase the photoactivity and lifetime of separated charges.[34] As mentioned above, electrochemical control gives a simple way to generate an internal electric field through the formation of a SCL. In ferroelectric materials, an internal electric field (polarization) is spontaneously generated due to the non-centrosymmetric distribution of ions. As a result, electron-hole charge separation is enhanced and charge recombination is suppressed, without the need for an applied bias. Epitaxial growth of ferroelectric BaTiO3 on TiO2 nanowires was shown to increase PEC performance.[35] The enhanced performance of the BaTiO3/TiO2 heterojunction was attributed to enhanced charge separation, although direct monitoring of charge carriers was not carried out. Using TAS to directly monitor charge carriers, Morris et al. compared the dynamics of BaTiO3 in the non-ferroelectric cubic phase to those of the ferroelectric tetragonal phase.[36] The internal electric field in ferroelectric BaTiO3 increased the charge carrier lifetime by 4 orders of magnitude (Figure 3). The charge carrier lifetime of the ferroelectric material was found to be roughly 0.1 s, approaching the typical rates of water oxidation seen on metal oxides, and should therefore be advantageous for photocatalytic water oxidation. Importantly, this long lifetime was obtained without applying a bias or using sacrificial reagents, demonstrating the potential of generating long-lived charge in ferroelectric materials. Recently, atomic-thick SnTe with ferroelectric properties at room temperature has been discovered,[37] and may facilitate the incorporation of ferroelectric layers in photocatalytic systems to promote charge separation. The surface chemistry of ferroelectric materials are also predicted to be influenced by the polarisation and may introduce additional control to accelerate desired photocatalytic reactions.[38]

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Figure 3. TAS decays of ferroelectric BaTiO3 (blue line) shows significantly longer lifetime compared to non-ferroelectric BaTiO3 (red and black lines). Reproduced from [36].

The formation of heterojunctions between different semiconductors or semiconductors and metals has also proved to be beneficial in separating charges.[17] Interfacial electric fields can contribute to the energetic considerations that drives opposite charges to different materials and enables effective charge separation. Since multiple charge transfer steps can occur in such heterojunctions, detailed investigation of the charge carrier dynamics in addition to comparing the performance is critical to verify the impact of the junction on the possible charge transfers pathways.[39-43] Yang et al. turned to transient photoreflectance to monitor p-GaInP2 junctions with Pt or TiO2.[44] Inspection of the oscillations in the photoreflectance spectra allowed the determination of both the magnitude of the built-in electric field at the junction as well as the time-dependant changes of these electric field after photoexcitation. Longer lifetimes of the charge separated state were observed with TiO2 junctions compared to Pt, assigned to an increased barrier height to charge recombination and increased width of the depletion region (Figure 4). Inorganic (hetero)nanostructures of semiconductors such as CdS and CdSe allow for precise control of exciton and charge carrier dynamics and can show external quantum efficiencies for H2 production of over 50%[45] using Earth-abundant catalyst.[46] We refer the reader to a recent comprehensive review of this field which emphasises the mechanistic insights gained from time-resolved spectroscopies.[47]

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Figure 4. Energy band diagram obtained by transient photoreflectance indicating charge flow. Recombination across the p-GaInP2/TiO2 p-n junction (~ 100 ns) is slowed down in part by the larger barrier (> 0.56 eV) that needs to be overcome compared to the p-GaInP2/Pt Schottky junction (~ 10 ns; 0.3 eV barrier) From ref. [44]. Reprinted with permission from AAAS.

Forming heterojunctions of plasmonic metals in contact with metal oxides has been established as another viable route to improve the efficiency of photocatalytic processes.[48] Visible light excites the plasmon resonance and plasmon-mediated electron transfer (PMET) can inject a high energy electron into the CB of the semiconductor.[49] DuChene et al. performed photoelectrical characterisation of Au/TiO2 heterostructures and discovered that the lifetime of electrons generated via PMET is 1-2 orders of magnitude longer than what is observed after direct UV-excitation of TiO2.[50] The extended lifetime was rationalised by spatial separation of electrons in TiO2 and holes in Au, as well as the formation of a Schottky barrier with rectifying properties that impedes back electron transfer from TiO2 to Au. Visible light photocatalytic activity confirmed that PMET produces reactive charges for the production of H2. Plasmonic junctions with a ferroelectric material have also recently been reported. Ferroelectric material layers were incorporated to nano-Au arrays, and the PEC performance of these photoelectrodes could be controlled by the ferroelectric polarisation.[51] Transient absorption spectroscopy monitored the kinetics of Au-based transitions, and surprisingly found faster decay rates in the best performing configuration. Efficient charge injection was proposed to be responsible in accelerating relaxation to the ground state. Further kinetic investigations of the effect of electric fields on PMET, for example by monitoring the electrons injected into the semiconductor, are warranted to understand the working principles of such systems.

Dye-sensitized photoelectrosynthesis cells based on dye-sensitised TiO2 or SnO2, with analogy to dye-sensitised solar cells (DSSCs),[52, 53] have also been shown to be a viable approach to solar fuel production.[54, 55] Spatial charge separation is driven by the favourable energetics for charge transfer in donor-acceptor type dyads. Typically, a molecular catalyst is used for the water oxidation, while electrons are injected into TiO2 and relayed to a Pt counter electrode by an external circuit. However, kinetic challenges remain and need to be overcome. The mismatch in rates between electron diffusion within the metal oxide and charge recombination (both processes take place on the μs – ms timescales) severely limits the accumulation of oxidation equivalents at the water oxidation catalyst.[54] Dye-sensitized H2 producing systems have also been assembled, making use of molecular reduction catalysts.[56] A study using transient optical spectroscopies established the recombination and charge transfer timescales and concluded that the mechanism of reaction (oxidative vs reductive quenching of the dye excited state) may change depending on the system assembly.[57] The same Ni-based proton reduction catalyst was also effectively used with carbon nitride photocatalyst, where defect engineering resulted in improved charge transfer efficiency on the sub-μs timescale forming a value-added aldehyde product and photogenerated electron lifetime on the order of hours.[58, 59]

**Structural Considerations**

In hopes of tuning the catalytic function of reactive sites to improve water oxidation kinetics, structural characterisation of the reactive intermediates involved in the charge transfer reaction should prove very informative. While optical absorption based techniques may provide some basic structural information, for example the formation of an Fe4+ intermediate state in the water oxidation reaction on hematite,[60] other (in operando) techniques are needed to obtain detailed structural characterisation. The use of time-resolved XPS techniques holds promise to simultaneously probe charge carrier dynamics of a semiconductor substrate and the electronic configuration of surface-bound molecules, such as sensitiser dyes.[61] In operando X-ray scattering study of Pt electrocatalyst revealed the structural development of the surface as well as oxide formation under oxidative conditions.[62] Infrared spectroscopy has recently been used to identify water oxidation intermediates on hematite photoelectrodes (FeIV=O)[63] and Co3O4 nanoparticles (superoxide intermediate and CoIV=O).[7] Direct comparison of picosecond dynamics in SrTiO3 in visible and IR probe regions allowed for the powerful combination of charge carrier dynamics and structural identity of the oxidative equivalents formed at the surface.[64] A nonadiabatic kinetic mechanism was proposed to explain the formation of two types of O-site radicals, Ti-O• oxyl and Ti-O•-Ti bridge, as valence band holes are trapped at the aqueous interface with a 1.3 ps time constant. Similar combined charge carrier and structural investigations of promising photocatalytic systems should provide significant information for the development of rapid interfacial charge transfer reactions.

**Conclusions**

Key to the functioning of solar energy conversion devices is the kinetic competition of productive steps versus charge recombination. This kinetic challenge is magnified in solar fuel producing photosystems as interfacial charge transfer typically occurs on long timescales (millisecond – second). Strategies are thus needed to increase the charge carrier lifetime, and various approaches have proved to be promising: increased space charge layer width from potentiostatic control, internal electric field in ferroelectric materials, heterojunction formation with metal oxides or plasmonic metals, donor-acceptor dyads. Detailed investigations of the charge carrier dynamics of novel materials, such as promising photocatalyst sheets[65] and organic polymer systems,[66] has the potential to lay out the basis for design rules that will accelerate future developments in solar fuel production. Reducing the impact of recombination may also be accomplished by accelerating interfacial charge transfer kinetics. While difficult in practice, recent efforts in structural characterisation of reactive intermediates should prove fruitful in developing novel, highly active catalytic sites.

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**Papers of special interest\***

Time-resolved infrared structural investigation of water oxidation intermediates on cobalt oxide nanoparticle catalyst show the presence of superoxide and oxo-based species.[7]

Transient absorption spectroscopy of hematite photoanode under operating conditions reveal bias-dependant bulk recombination and yield of long-lived surface holes.[22]

Demonstration that cocatalyst and passivation layers affect the charge carrier dynamics of hematite photoanodes in a similar fashion.[28]

Transient open circuit voltage decay experiments determine that electrons generated via plasmon-mediated electron transfer in Au/TiO2 heterojunctions show 1-2 orders of magnitude longer lifetimes compared to those generated via direct excitation of TiO2.[50]

Infrared investigation of water oxidation by hematite photoanodes provides direct evidence of surface iron oxo intermediate during operation.[63]

**Papers of outstanding interest\*\***

In situ time-resolved photoluminescence strategy to determine the bias-dependent quantum yield of charges reaching the semiconductor/electrolyte interface.[27]

Detailed investigation of the role of a CoPi cocatalyst layer on BiVO4 reveals that the major water oxidation pathway does not involve the cocatalyst due to slow water oxidation and hole transfer to CoPi.[33]

Demonstration that internal electric fields from ferroelectric polarization increases charge carrier lifetime by 4 orders of magnitude in BaTiO3.[36]

Ultrafast transient photoreflectance spectroscopy probes interfacial charge carrier dynamics at junctions and shows an order of magnitude reduction in recombination rate when a p-n junction is formed compared to a Schottky junction.[44]

Comprehensive review of charge carrier dynamics and mechanistic insights into the working principle of semiconducting nanorod heterostructures for solar-to-fuels applications.[47]

Combined visible and IR transient absorption spectroscopies are used to probe the transfer of valence band holes to the surface and the formation of oxyl and bridge radicals in SrTiO3.[64]

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