# Photocatalysis: Basic Principles, Diverse Forms of Implementations and Emerging Scientific Opportunities

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**Photocatalysis promises a solution to challenges associated with the intermittent nature of sunlight which is considered as renewable and ultimate energy source to power activities on Earth. This review aims to provide a broad overview of the field. Insight into natural photosynthesis is discussed first, which provides a scientific basis for most efforts on photocatalysis. Afterwards, the details of four existing types of photocatalysis are presented, namely photosynthesis by plants, photosynthesis by microalgae, photocatalysis by suspension and photoelectrocatalysis. Detailed analyses of simple photocatalysts and integrated photocatalytic systems are followed to shed light on the different functionalities of different components in a working photocatalyst. Special attention is given to the roles played by surface and interface chemical phenomena. Lastly, perspectives on artificial photosynthesis are discussed briefly at the end.**

## 1. Introduction

As the main energy source delivered from the extraterrestrial space, solar energy promises to surpass the annual global energy demand by a large margin.[1] Given the long predicted lifetime of the Sun, solar energy is also considered the ultimate renewable source that we can harvest on the planet of Earth.[2] The diurnal and intermittent nature of this energy source, nonetheless, presents significant challenges in terms of harvesting, storage and utilization.[3] Presently, there are a number of technologies in place that may be used to meet the challenges. For instance, solar energy can be directly collected, converted and stored in the form of heat, which can either provide heat to residence or be further converted into electricity (as well as other forms of energy).[4] The most studied technologies concerning solar photon harvesting may be on those by the photovoltaic effect, the discovery of which has been credited to Edmond Becquerel dated back to 1839.[5] While the development of the semiconductor theory and practice has greatly advanced this branch of technology, and large-scale production of solar panels (mostly enabled by crystalline Si) continue to dominate the market, how to cost-effectively store the electricity remains a grand challenge.[6] Another well-studied route of solar energy harvesting and storage concerns photochemical reactions.[7] The rationale is that chemical bonds are convenient media for energy storage. Indeed, if we consider the 21% of $O_2$ in the atmosphere is mostly biological $O_2$ owing to natural photosynthesis, the scale of energy stored by chemical reactions over billions of years of evolution is enormous, far exceeding what can be measured by known fossil fuel reserves. The recognition of this fact has inspired generations of scientists to learn from natural photosynthesis and ultimately to develop technologies much more efficient and less costly than natural photosynthesis to meet our ever-growing energy needs.[8] Nevertheless, it is important to note that the overarching research of photosynthesis has broader impacts beyond solar energy storage. How to use the energy delivered by photons instead of heat to enable and/or power chemical reactions is interesting in its own right. This branch of research has been broadly referred to as photocatalysis in the literature.[9] Our goal of writing this review article is to provide a broad overview of this field. We aim to offer a historical account of the development of photocatalysis, its current status, and possible future directions. Most important of all, we hope to unify some often-confusing concepts surrounding the keyword of photocatalysis and provide the readers an opportunity to focus on the important common scientific merits of seemingly different approaches. The article is organized in the following ways. We start with basic principles that govern photosynthesis and then move on to introduce the historical view of photocatalysis. Existing variations of photocatalytic reactions are next summarized, followed by discussions on integrated systems where components with distinct functionalities are presented. Afterwards, the article examines the importance of interfaces between different components within an integrated system. At the end of the review, we present our perspectives on where the field is headed.

## 2. Lessons from the Nature

Photosynthesis refers to the process by which green plants, microalgae and some forms of bacteria harvest the energy from

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the sunlight to power thermodynamically uphill reactions such as the conversion of $CO_2$ and $H_2O$ to carbohydrate.[10] While the detailed thermodynamic discussions will be presented later in this review (Section 3), it suffices here that these reactions are thermodynamically uphill, meaning that providing energy to power these reactions is critical. The detailed mechanisms of photosyntheses by these different organisms indeed vary, but they share some common fundamental underlying principles. We borrow the general form of oxygenic photosynthesis as shown in **Figure 1** to facilitate our discussions.[11] Using this mechanism, we discuss 3 important aspects of the process, namely the energy flow, the electron flow, and the detailed chemical reactions.

### 2.1. Energy Flow

As is true in any photosynthetic system, the most important aspect is how the energy from light is harvested and transferred. Figure 1 includes two key components, photosystem I, or PSI, and photosystem II, or PSII. Photons are absorbed by the pigments in these photosystems, where the energy is used to excite electrons. Collectively, these two photosystems harvest enough energy to power the reactions of $H_2O$ oxidation (on the site of PSII) and the synthesis of NADPH (on PSI). In the meanwhile, protons transfer across membrane coupled with electrons transfer (will be discussed in Section 2.2). As such, a (significant) portion of the harvested energy helps build a proton gradient (3–3.5 pH units, corresponding to a proton-motive force of 200 mV) across the thylakoid membrane, which will be used to power the synthesis of ATP.[12] Together, the ATP and NADPH are later used in the dark reactions (Calvin cycle) for the $CO_2$ fixation reactions.

### 2.2. Electron Flow

Excited electrons are the main vehicles in photosynthesis to carry the energy flow. They are extracted from the negatively charge O in $H_2O$ at the site of PSII during the light reactions. Once excited, they are quickly moved away from this site by a series of proteins as indicated by the green arrows in Figure 1, losing some of their energies in the process. Once they reach the PSI site, a second excitation takes place, providing enough energy for the electrons to enable the synthesis of NADPH. In many ways, NADPH can be regarded as a temporary electron storage medium (in the form of reduced protons). These stored electrons are ultimately transferred to $CO_2$ during the dark reactions to complete their journey from $H_2O$ to $CO_2$.

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### 2.3. Main Chemical Processes in Oxygenic Photosynthesis

Figure 1 only shows one of the two important stages of natural photosynthesis, the light reactions. Here the chlorophylls in PSII absorb photons to enable charge separation for the creation of $P_{680}^{+}$—$Pheo^{-}$.[13] The concerted activity of the oxygen

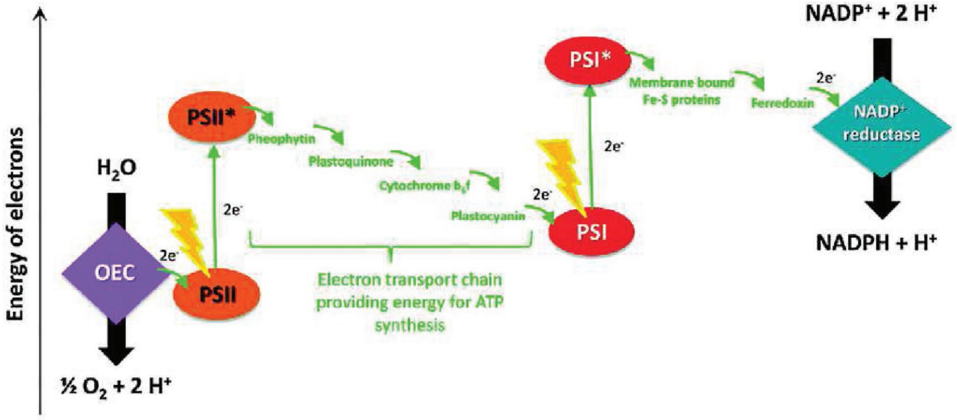


**Figure 1.** Schematic representation of natural photosynthesis. Reproduced with permission.[11] Copyright 2014, The Royal Society of Chemistry.

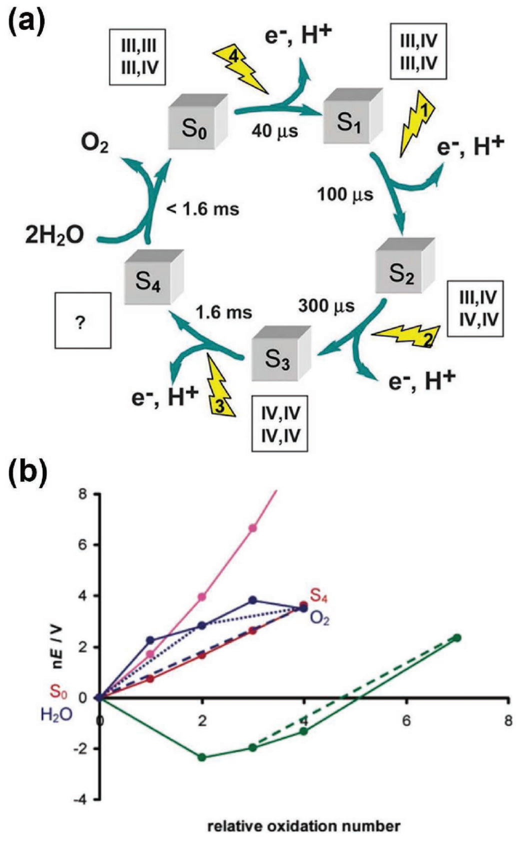


**Figure 2.** a) Schematic illustration of the five stages of OEC. Reproduced with permission.[17] Copyright 2013, The Royal Society of Chemistry. b) Frost diagram for oxygen production half reactions at pH 6 vs NHE. Red line: OEC; blue long-dashed line: four-electron $S_4/S_0$ couple; blue short-dashed line: two electron couples, $S_4/S_2$ and $S_2/S_0$; blue solid line: $2H_2O$ (0), $H_2O$ + OH· (1), $H_2O_2$ (2), $O_2^{-\bullet}$ (3), and $O_2$ (4); green line: a single manganese ion; magenta line: a manganese tetramer hypothesized without PCET. Slopes of each line indicate driving force for water oxidation. Green and magenta line: proposed catalyst for water oxidation. Reproduced with permission.[20] Copyright 2006, The Royal Society of Chemistry.

evolving center (OEC, $Mn_4Ca$-cluster) is critical to the functionality of PSII. As will be seen in **Figure 2**a, $P_{680}^+$ oxidizes OEC stepwise, during which process $H_2O$ is oxidized by the activated OEC to molecular $O_2$ and $H^+$. Another area where rich chemistries take place is the PSI site, where light absorption induces the formation of the $P_{700}^+$—$A_0^-$ charge pair.[14] Of them, $P_{700}^+$ can be reduced by electrons supplied by PSII and further excited by PSI. $A_0^-$ will be used to reduce $NADP^+$ to NADPH. In parallel, the processes concentrate $H^+$ on one side (the bottom side in Figure 1) of the thylakoid membrane to build up a large concentration gradient, which is used by the ATPase to power the ATP synthesis.[12]

The light-induced processes can be represented as:

$$2H_2O + 4h\nu \rightarrow O_2 + 4H^+ + 4e^- \tag{1a}$$

$$2NADP^+ + 2H^+ + 4e^- + 4h\nu \rightarrow 2NADPH \tag{1b}$$

Together, the overall reaction may be written as:

$$12H_2O + 12NADP^+ + 48h\nu \rightarrow 6O_2 + 12NADPH + 12H^+ \tag{1}$$

What are not represented in Figure 1 are the dark reactions:

$$\begin{aligned} &6CO_2 + 12NADPH + 18ATP + 12H^+ \\ &\quad \rightarrow C_6H_{12}O_6 + 12NADP^+ + 18ADP + 18p_i + 6H_2O \end{aligned} \tag{2}$$

where $p_i$ is inorganic phosphate.[15] Of these chemical reactions, we wish to particularly point out the details of water oxidation (Equation (1a)). It is important because it is the first step of natural photosynthesis which supplies electrons for the subsequent reduction reactions. The electrons can be used for $CO_2$ fixation. They can also be used for direct $H^+$ reduction which enables solar $H_2$ synthesis. The reaction is also important because its 4-electron, 4-proton nature renders it the rate determining step (RDS) in many photosynthetic reactions. The understanding of its chemical mechanisms holds the key to a large number of processes that are currently being developed. For instance, the main limiting factor of solar hydrogen production is the lack of suitable photoanodes for water oxidation with good performance in terms of kinetics and stability to match that of the photocathodes.[16] Studies of the OEC of PSII reveal that it consists of one Ca atom and four Mn atoms in a $Mn_4Ca^{2+}$ complex.[17] The complex can be oxidized by PSII through a series of proton-coupled electron transfer (PCET) processes in four steps, from $S_0$ to $S_4$ (Figure 2a). $S_4$ can be turned over to $S_0$ by oxidizing $H_2O$ to liberate $O_2$.[17,18]

To date, the design principles represented by Figure 1 are the only ones demonstrating large-scale successes in operation. As such, much can be learned from this model in developing artificial photosynthesis systems. From the simplified discussions presented above, we gain several important insights into the design principles. First and foremost, the system is an integrated complex system. Components of different, and often well-defined, functionalities are needed. For instance, the roles of the light absorbers and charge separation mechanisms are distinct and easy to distinguish. Second, we see that the balance between stability and reactivity is critical. Consider the OEC as an example. As a RDS in the light reactions, the activity of the catalytic centers is critically important. However, these active centers are by definition also highly unstable. The natural photosystems protect these centers with a large group of proteins and repair the OEC continuously.[17] Third, well-controlled energy and electron flows are of fundamental importance. In the natural photosystems, this is achieved through precise arrangements of functional proteins buried in the thylakoid membrane. Similar arrangements of different functional groups in an artificial system will likely be equally important. The remainder of the review is guided by these insights.

### 2.4. Thermodynamic Analysis

An intriguing question to ask about the natural photosystems is why two light absorbers are needed. Intuitively, we see the needs arise from the reducing powers necessary to complete the water splitting reactions. Let us take a look at Figure 1 again. At neutral pH (pH ≈ 7), the dual photosystems provide a photovoltage to match the redox reaction ($O_2/H_2O$: 0.82 V vs NHE and NADP$^+$/NADPH: −0.32 V vs NHE, where NHE stands for Normal Hydrogen Electrode as a reference).[13] The reactions should be possible if we have a single photosystem that provides much greater energy than the natural PSI and PSII combined, enough to power the overall reactions. Indeed, detailed thermodynamic balance has been utilized to study the different scenarios consisting of varying numbers of lighter absorbers, including the single-absorber possibility.[19] It was found that from an efficiency perspective, higher efficiencies are expected when more light absorbers are involved. When one takes into account that the system would be too complex to balance when more light absorbers are involved, 2-absorber systems would almost be the ideal compromise. We see from this point the ingenuity of the natural photosystems. In other words, when regarded as an engineered system, the natural photosystems are optimized. Similar conclusions can be drawn when one looks at the detailed energy landscapes of the OEC of the PSII as shown in Figure 2b.[20] As a consecutive 4-electron, 4-proton process, the relative energy levels of the intermediate states ($S_0$, $S_1$, $S_2$, $S_3$ and $S_4$) are shown in red solid dots connected by the red solid line. Any deviations from this line present some forms of challenges. Consider the blue solid line as an example. The driving force (as measured by the slope of the energy vs the oxidation number) of the first step would be so high that it would promote the formation of hydroxide radical (OH·). Similarly, during the second step of the process outlined by the solid-blue line, the formation of $H_2O_2$ would prevail, followed by $O_2^{-\bullet}$ formation during the third step. This possible route presents at least two critical issues. First, greater energy would be needed as the intermediates are of higher energies. Second, highly reactive byproducts would be produced. Next, we can look at the importance of PCET. If we follow the magenta line in Figure 2b, we see that significantly greater energy would be needed if electron transfer is not coupled by proton transfer. Lastly, we also see the importance of the OEC complex by looking at the green lines, where much higher oxidation states of the Mn active center would be needed for the oxidation of $H_2O$. Taken as a whole, we come to appreciate the optimization of the natural photosystems and further realize how important it is to learn from the successful example when designing artificial systems.

## 3. Photocatalysis

In this section, our goal is to provide a broad definition of photocatalysis as it has been interchangeably used in the literature, creating considerable confusion when the terminology is not treated with care. As will be seen next, the development of photocatalysis was indeed inspired by natural photosynthesis. From this perspective, it should be fair to regard thermodynamically uphill reactions powered by light as photocatalysis (**Figure 3**a). However, a source of confusion may come from the uphill thermodynamic nature itself. In catalysis, such reactions are not spontaneous.[21] Hence, the introduction of a canonical "catalyst" is not expected to enable a nonspontaneous reaction. To reconcile the discrepancies in the terminology, it is not uncommon in the literature where authors regard light as a reactant, which would alter the view of the system's thermodynamics to permit the broad application of "photocatalysis" to describe such systems.[9,22] In parallel, there are a large number of chemical reactions that are spontaneous whose kinetics is hindered by the high activation energies (such as pollutant oxidation; Figure 3b).[23] Here the introduction of light to enable the reaction falls in the canonical definition of catalysis. As a result, photocatalysis would be an ideal terminology to describe such reactions. Additionally, a less obvious class of reactions that also often borrow the keyword photocatalysis are those require externally applied potentials. They are variably referred to as photoelectrochemical or photoelectrocatalytical reactions in the literature.[24] Our view is that the fundamental processes involved in these reactions are the same should it be photosynthesis or canonical photocatalysis. Consequently, they should be treated as the same group of reactions for the benefit of understanding and further development.

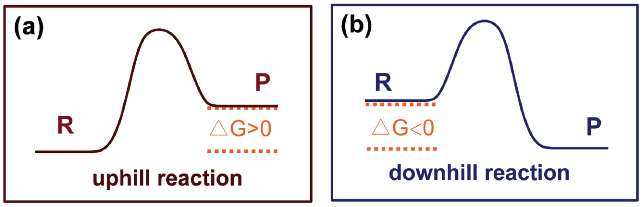


**Figure 3.** Thermodynamic illustration of photocatalysis. a) Uphill reactions, b) downhill reactions. R: reactants, P: products.

### 3.1. History of Photocatalysis

As early as 1901, chemist Giacomo Ciamician was one of the first to conduct experiments to study whether "light and light alone" would enable chemical reactions.[25] He carried out experiments with blue and red lights and found that a chemical effect took place only in blue light. He was careful enough to exclude the possibility that these reactions were instead powered by thermal heating induced by light. In 1911, the keyword "photocatalysis" first appeared in scientific literatures.[26] Scientists referred to Prussian blue bleaching by ZnO under illumination photocatalysis. This observation has inspired subsequent experiments of using ZnO as a photocatalyst for other reactions such as the reduction of Ag$^+$ to Ag under irradiation in 1924.[27] It is noted that although photosensitive reactions had been long discovered prior to these efforts, those processes did not involve a light-sensitive catalyst.[28] Later, $TiO_2$ and $Nb_2O_5$ were reported to drive photocatalytic reduction of $AgNO_3$ to Ag and $AuCl_3$ to Au in 1932.[29] Afterwards, $TiO_2$ was investigated in 1938 as a photosensitizer to bleach dyes in the presence of $O_2$.[30] Nevertheless, interests in photocatalysis remained a hobby due to the absence of mainstream practical applications. The situations changed in the early 1970s for two reasons. First, the "oil crisis" prompted scientists to seek alternative energy supplies to fossil fuels.[31] Second, the concerns over environmental impacts by large-scale industrial operations motivated researchers to search for renewable energy sources.[9] Several seminal papers were published during this period of time. In 1968, scientists from the Bell Lab first reported $O_2$ evolution on $TiO_2$.[32] In 1972, Fujishima and Honda reported photo-assisted

$H_2O$ oxidation with $H_2$ production using $TiO_2$ electrodes under UV light irradiation.[33] Photocatalytic water splitting without external energy input other than light yielding $H_2$ and $O_2$ under argon in stoichiometric ratio of 2:1 was reported in 1977.[34] Interestingly, this work found that $O_2$ formed but $H_2$ evolution was inhibited in the presence of $N_2$. The authors concluded that $N_2$ was reduced to $NH_3$ and trace amount of $N_2H_4$ by $TiO_2$. During the same period of time, Frank and Bard first reported the decomposition of $CN^-$ and $SO_3^{2-}$ by $TiO_2$, ZnO, and CdS under light.[35] Later, Fujishima et al. reported studies on photocatalytic $CO_2$ reduction using various inorganic semiconductors as photocatalysts in 1979.[36] These early efforts extended the applications of photocatalysis, drawing significant research attention in the 1980's to similar reactions using, in particular, $TiO_2$ nanoparticles as the photocatalysts.[37] Since then, investigations have been concentrated on understanding the fundamental principles, enhancing the photocatalytic efficiencies, searching for new photocatalysts, and expanding the scope of the reactions. For instance, photo-induced super-hydrophilicity effect was discovered on $TiO_2$ in 1997.[38] As a result, $TiO_2$ with self-cleaning and anti-fogging functionalities has been applied to building materials.[39] In the development of new photocatalysts, many candidates with higher photocatalytic activities than $TiO_2$ have been studied, most featuring wide bandgaps and only active under UV lights.[40] For higher efficiencies, visible light absorbing photocatalysts have been pursued in parallel.[41] In the meanwhile, researchers gradually learned more about the principles that govern photocatalysis, which will be discussed later in this review (Sections 5, 6, and 7).

### 3.2. Broad Definition of Photocatalysis

Photocatalysis, while varying in details in terms of reactions and mechanisms, may be described by four important steps (shown in **Figure 4**): (I) light absorption to generate electron-hole pairs; (II) separation of excited charges; (III) transfer of electrons and holes to the surface of photocatalysts; and (IV) utilization of charges on the surface for redox reactions. For the third step, a large portion of electron-hole pairs recombine, either en route to the surface or on the surface sites.[24c,42] The recombination dissipates the harvested energy in the form of heat (nonradiative recombination) or light emission (radiative recombination).[43] The long-lived photogenerated charges on the surface have the potential to promote different redox reactions, the details of which depend on the donor or acceptor properties of the surface absorbed species.

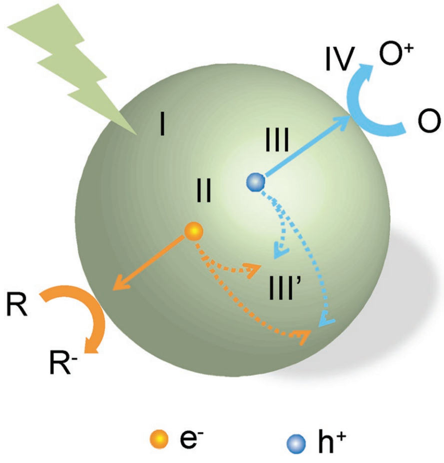


**Figure 4.** Steps in photocatalytic reaction process. R: chemicals in reductive reactions, O: chemicals in oxidative reactions. (I) light absorption to generate electron-hole pairs; (II) separation of excited charges; (III) transfer of electrons and holes to the surface of photocatalysts; (III′) recombination of electrons and holes; (IV) utilization of charges on the surface for redox reactions.

As discussed above, what conforms to the canonical definition of "catalysis" would be photocatalysis of organic pollutant degradation, where the reaction would be spontaneous from a thermodynamic perspective.[21] The introduction of a photocatalyst would alter the reaction route and thus improve the kinetics. The topic has been studied extensively and has been reviewed previously.[44] In this review, we wish to put an emphasis on the photosynthetic reactions that are inherently non-spontaneous without the energy input of light. The new round of research efforts over the past decade on this topic has been motivated by the rapidly growing need for large-scale solar energy storage.[45] The Gibbs free energy changes of a few representative chemical reactions of interest in this category are shown in **Figure 5**.[46] Due to the similarities of these reactions to natural photosynthesis, these reactions are commonly referred to as artificial photosynthesis in the literatures.[47] Note that here we take a broad view of what photosynthesis means. In some literature, it may be specifically tied to reactions involving water splitting and $CO_2$ reduction. Among the reactions shown in Figure 5, water splitting produces hydrogen, which is a posterchild of renewable (or clean) energy. It has arguably received the most research attention.[48] The reaction is indeed fundamentally important because it is also the first step in natural photosynthesis (see Section 2.3) where electrons are extracted from $H_2O$ for the subsequent reduction reactions. The interest in $CO_2$ reduction is self-evident given that $CO_2$ is the key culprit in today's global warming discussions.[49] From a chemistry standpoint, the reduction of $CO_2$ is also tremendously interesting because it can involve up to 8 electrons and 8 protons in a one-carbon pathway (in the formation of $CH_4$, for instance) and more than 8 electrons in two or three-carbon pathways.[50] The complexity and the many different possibilities in product formation provide a fertile field to test various

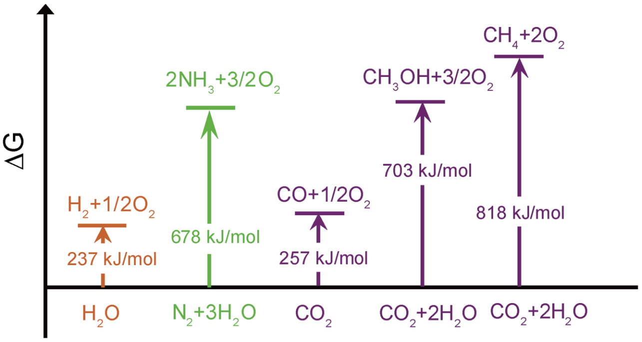


**Figure 5.** Energy diagrams of representative thermodynamically uphill reactions.

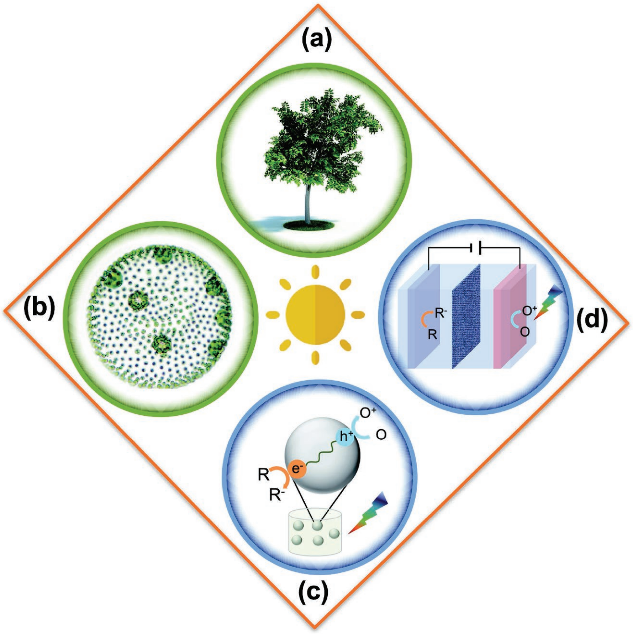


**Figure 6.** Types of photocatalytic reactions. a) Natural photosynthesis in plants, b) photosynthesis by microalgae, c) nanoparticles photocatalysis, d) photoelectrocatalysis.

chemical theories. The formation of valuable chemical products such as $NH_3$ and various alcohols represents a key issue in modern chemical industry. How to carry out these processes with significantly reduced cost and/or energy input constitutes a grand challenge that has enormous economic implications.

## 4. Summary of Existing Photocatalysis Reaction Types

In an effort to categorize existing approaches of photocatalysis, we present in **Figure 6** four classes of reactions. In the first category (Figure 6a), we see the most successful photocatalysis, natural photosynthesis. An ingenious result of billions of years of evolution by Mother Nature, the process has been the main source of our energy supply. Carbohydrates are the key products of these reactions.[51] A variation of this reaction is shown in Figure 6b, where microalgae perform reactions similar to those in plants but synthesize unique chemicals such as $H_2$ or other valuable chemicals (e.g., ethanol, butanol, glycerol, and isoprene).[51,52] When it comes to artificial photosynthesis systems, a great number of variations exist. They may be grouped into two general types as summarized in Figure 6c and 6d. When the reduction and oxidation reactions are not intentionally separated (Figure 6c), a system with the benefit of inherently low cost is obtained. Note that reactions involving both heterogeneous and homogeneous catalysts can be included in this category. A competing strategy is to physically separate the reduction and oxidation sites. A wired version of the last strategy is shown in Figure 6d. But the wire is not essential here. A back-to-back wireless configuration falls in the same category, as well.[53] A key distinguishing feature of Figure 6c and 6d is whether the reduction and oxidation sites are physically separated by a reasonable distance (greater than a few hundred nanometers).[54]

### 4.1. Photosynthesis by Plants

In plant photosynthesis, the energy delivered by sunlight is absorbed by chlorophylls to power the conversion of $CO_2$ and $H_2O$ into carbohydrate, with the production of $O_2$. It produces food (either directly or indirectly via animal products), oxygen, and thermal energy for lives. The process is the ultimate source of energy supply for most fossil fuels, coal, oil and a large portion of natural gases. Plant photosynthesis also represents a main mechanism by which atmospheric $CO_2$ is consumed and reduced, balancing the global warming effect. While an incredible system in its own right, the natural photosynthesis system of plants is by no means optimized for efficiency. As a matter of fact, when the broad solar spectrum is considered, by only counting what portion of the energy is harvestable and useful, and by averaging over seasons and nights and days, we rarely see plants that are >1% in converting and storing solar energy.[55] The low overall efficiency leaves much room for improvement. Such room has been the key motivation for artificial photosynthesis.[56] Additional considerations for not over-exploiting plant photosynthesis to quench our thirst for energy include the competition of food production and the high cost associated with irrigation and soil depletion, among others.

### 4.2. Photosynthesis by Microalgae

Different from plants, microalgae are single cell microorganisms without roots, stems and leaves.[57] They present an opportunity for system engineering with a focus on the products without having to share the harvested solar energy with parasitic processes such as tissue formation. Moreover, microalgae can be placed at locations on non-arable lands and/or in marine environments.[58] Saline and wastewater, but not necessarily fresh water, can be directly fed to the system.[59] For these advantages, microalgae-based photosynthesis is favored for further developments. The most investigated application of microalgae-based photosynthesis is to produce $H_2$ from sunlight and $H_2O$.[60] This is because many microalgae can be genetically engineered to promote hydrogen metabolism. Electrons from PSII (as a result of water oxidation) are accepted by hydrogenase to directly reduce $H^+$ for the production of $H_2$.[51] In fact, the ease of genetic engineering renders microalgae a versatile platform for photosynthesis. For example, different synthase genes can be expressed in microalgae through heterologous transformation for the production of isoprene.[51] There, however, remains a long way to go before photosynthetic microorganisms can enable large scale, economical biofuel production. The relatively narrow absorption within the solar spectrum represents one challenge that has yet to be addressed.[61] Another challenge is the saturation effect, where the conversion efficiency does not scale with the increasing concentrations of microorganisms, limiting the overall efficiency of the system.[62]

### 4.3. Photocatalysis by Suspensions and/or Homogeneous Photocatalysis

#### *4.3.1. Heterogeneous Powdery Photocatalysis*

One of the least complicated applications of photocatalysis is to simply suspend photocatalysts in a solution and shine light on it. Often, the photocatalysts are nanoscale particles. In such a system, each photocatalyst nanoparticle may be regarded as an integrated system consisting of short-circuited photoanode and photocathode. Naturally, the ease of implementation offers the benefit of low cost. The simplicity, nevertheless, also introduces significant challenges, the most critical of which is the low efficiency.[63] Reasons for the low efficiency include severe recombination.[42b] Because the reduction and oxidation sites at the nanoscale in such an integrated system are often not well defined, the charge separation mechanisms are consequently not optimized, thereby resulting in charge recombination within an individual photocatalyst or on the surface or both. The close proximity of the reduction and oxidation sites provides ample opportunities for the reduction intermediates and/or products to be oxidized, and vice versa. Additionally, having a mixture of oxidizing and reducing products (e.g., $O_2$ and $H_2$) raises concerns over safety.[64] The separation of the mixture later incurs additional cost.

Next, we focus on two aspects of the photocatalytic processes to illustrate that it is beneficial to keep the photocatalyst sizes in the nanoscale. Domen et al. calculated the relationship between photon absorption and photocatalyst sizes by assuming photocatalyst with a spherical shape.[65] Light intensity of AM 1.5G for photons with wavelength ranging from 280 to 600 nm was used for the estimate. As the diameter of the photocatalyst grew larger, the number of photons striking the photocatalyst per second was greater. Consequently, the time interval between photon strikes was smaller. For instance, the average time between photon strikes for a 50 nm particle would be $5.6 \times 10^{-1}$ µs; that for a 5 µm particle would be $5.6 \times 10^{-5}$ µs. Given that the time it takes for surface chemical reactions to complete is typically longer than µs, it should be beneficial to choose photocatalyt sizes to allow for longer durations between photon strikes. In other words, it is desired to keep the photocatalyst sizes small.

Second, from the standpoint of reducing bulk recombination, it is desired to keep the photocatlyst small. The smaller the photocatalyst, the fewer grain/crystal boundaries within the bulk of the particle and, hence, less bulk recombination.[66] The benefits offered by small photocatalyst sizes are counterbalanced by issues connected to the small sizes. For example, smaller particles tend to aggregate more easily, presenting issues of poor suspension.[67] Higher surface areas inherent to smaller particles also mean greater surface recombination.[68] The expectations on how the photocatalytic activities would depend on the sizes of the photocatalyst have indeed been confirmed by prototypical studies on $TiO_2$.[69]

A variation of particle-based photocatalysis is to immobilize the photocatalysts on a support.[68b] The idea is to address the issues connected to the removal/recovery of the nanoscale photocatalyst while maintaining the benefits. Such issues can be significant where the removal of the photocatalyst is important but too difficult or too expensive or both. In addition, light scattering by photocatalyst particles near the light source limits light penetration in the solution for a suspension system, leading to insufficient photocatalyst utilization. In an immobilized powdery photocatalyst system, the substrate does not necessarily have to participate in the photocatalytic reactions. It can merely serve as a support. The strategy not only facilitates photocatalysis in liquid solution but also opens up the possibility of carrying out photocatalysis in the gas phase.[70] As shown in **Figure 7**, $TiO_2$ photocatalyst was immobilized on $\beta$-SiC foam with a high open porosity structure, which benefited larger loading amount of $TiO_2$ and air flow during gas phase photocatalytic reaction.[71]

#### *4.3.2. Homogeneous Molecule Photocatalysis*

As far as photocatalysis is concerned, the light absorbing and/or catalytic units can also be homogeneous molecules dissolved in $H_2O$ (or another medium).[72] Under light irradiation, a molecular photocatalyst (Pcat) can be promoted to the excited state (Pcat*) (**Figure 8**).[73] The typical result is electrons excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), similar to how electrons are excited from the valence band to the conduction band in semiconducting solid photocatalysts. The excited state Pcat* is both a strong reductant and a strong oxidant. Ideally, it can drive full redox reactions such as water splitting. In reality,

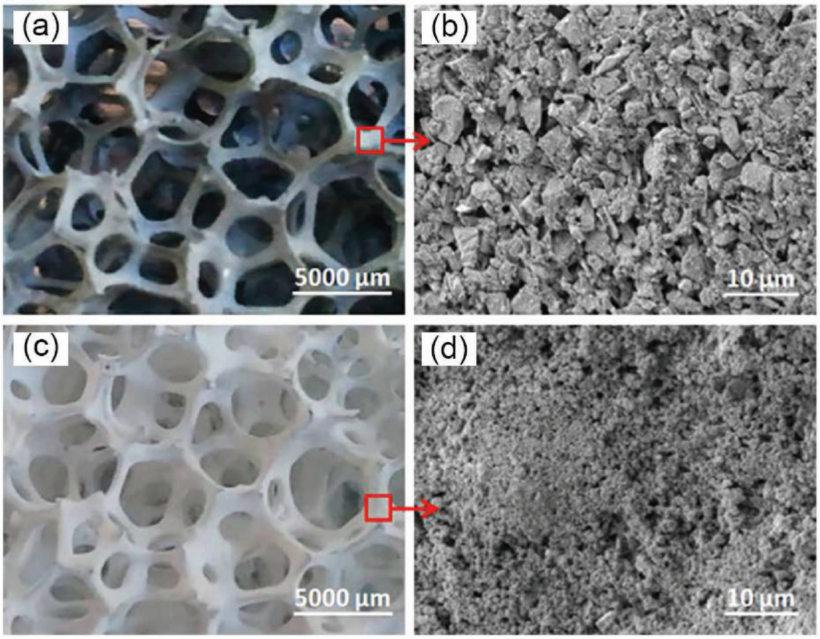


**Figure 7.** Optical and SEM images of bare $\beta$-SiC foam a,b) and $TiO_2$/$\beta$-SiC foam c,d). Reproduced with permission.[71] Copyright 2015, Elsevier.

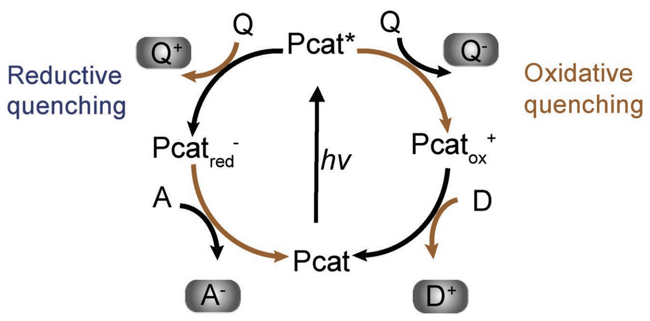


**Figure 8.** Photoredox catalysis by homogeneous photocatalyst. The oxidation steps are depicted on the right; the reduction steps are shown on the left. Pcat: photocatalyst, Q: quencher, D: donor, A: acceptor. Reproduced with permission.[73] Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

a sacrificial quencher (Q) is often necessary to yield a reduced species Pcat$^-$ and an oxidized species Q$^+$ in the case of reductive quenching, or a pair of Pcat$^+$ and Q$^-$ in the case of oxidative quenching (Figure 8).[73] In the former case, the reduced compound Pcat$^-$ then interacts with the reactants. And in the latter case, Pcat$^+$ oxidizes the reactants to higher oxidation states. A good example of such a system is found in polyoxometalates (POMs), which have been investigated as photocatalysts for water oxidation, degradation of organic pollutants, and removal of metal ions in water.[74] Another example of homogeneous photocatalyst is metal complexes such as $Re(CO)_3(bpy)^+$ -based complexes, which have been studied for photocatalytic $CO_2$ reduction.[75] Similarly, the $[Ru(bpy)_3]^{2+}$ family complexes have been investigated for water oxidation.[72b,76] Notwithstanding, at least three important challenges need to be addressed before homogeneous photocatalysts can be more widely used. First, the solubility of the photocatalysts makes it difficult to separate them from the solution after reaction either for reuse or for the purification of products or both. Second, homogeneous molecules with well-defined HOMO–LUMO separations often absorb narrowly within the solar spectrum. For exmple, most POMs only absorb 5% of the solar light due to the large separation between HOMO and LUMO.[77] Third, the photocatalytic activity and stability of homogeneous photocatalysts are limited by the instability inherent to the molecular nature of their structures.[76b,78] In the tests, precipitation is indeed frequently observed due to the decomposition of the photocatalysts.[79] Finding homogeneous photocatalysts that are stable and can absorb broadly in the solar spectrum is of great importance.[80] In recent years, many efforts have been devoted to heterogenizing homogeneous photocatalysts onto solid substrate (e.g., $TiO_2$, $SiO_2$, and g-$C_3N_4$) by adsorption, grafting, and/or electrostatic interaction to achieve better performance.[8,81] In such an immobilization strategy, molecular photocatalysts act as additional light absorbers or co-catalyst with active centers or both. This kind of integrated photocatalysis system will be discussed later in this review (Section 6).

#### *4.3.3. Full Reactions and Half Reactions*

The majority of studied photocatalytic reactions are redox reactions, meaning that there are oxidants and reductants in the system. While the oxidants and reductants may co-exist, as is seen in many homogeneous and powdery heterogeneous photocatalysis systems, or are well separated, as will be seen in the next section, the complete reactions require both to function as desired. Otherwise, the overall reaction would not be balanced and, hence, non-sustainable. Consider water splitting as an example. In a simplified form, $H_2O$ is being oxidized and reduced at the same time, producing reduced product of $H_2$ and oxidized product of $O_2$. In many photocatalysis systems, particularly the nanoparticle-based ones, the oxidation and reduction sites are often poorly understood. The lack of detailed information has been an important reason why full photocatalytic water splitting remains low efficiency. After all, it is exceedingly difficult to balance both thermodynamics and kinetics of two fundamentally different types of reactions at the same time. In the literature, it is a common practice to introduce sacrificial reagents that would either provide electrons or holes to facilitate the overall reactions. For example, alcohols are frequently used as a sacrificial reductant to donate electrons for photocatalytic $H_2$ generation studies.[82] Such approach circumvents the challenges associated with OER. Likewise, electron scavengers such as $AgNO_3$ are often used to enable studies of OER without worrying about the HER reactions.[83] In canonical photochemistry studies, chemical oxidants are also used to replace photosensitizers to enable the chemical processes without light, providing convenience as well as chemical insights.[84] However, knowledge generated by these substitutes is not always transferrable to the real photochemical full reactions.[66b,85] It is critical to note here that it has almost become a common practice to call some of these substituted reactions as "solar hydrogen production" in the literature. While it is strictly not wrong to do so, the practice can be misleading because the presence of sacrificial reagents would make the overall performance artificially better than the real water splitting reaction. As a result, the practice would make it subsequently difficult to highlight results from efforts focused on solving key issues in the true water splitting reactions, which is badly needed at the current stage.

### 4.4. Photoelectrocatalysis

Photoelectrocatalysis is also variably referred to as photoelectrochemistry (PEC) in the literature. The essence of this approach is to combine heterogeneous photoactive catalysts with electrochemical apparatus. This approach offers several distinct advantages. First and foremost, by separating the reduction and oxidation sites, PEC greatly limits impacts by issues connected to product crossover. As a result, much higher efficiencies than simple powdery photocatalysis are expected. Second, the quantitative measure of the number of charge (current) and their relative energies (voltage or potential) provides insights into the principles underpinning the function of photocatalysts. From this perspective, PEC is not only an engineering design for practical photocatalysis, but also serves as a characterization tool to understand the photocatalysts. Many advances made in electrochemistry can be readily borrowed to characterize photocatalysts in a quantitative fashion. Rich thermodynamic and kinetic information has indeed been collected using PEC techniques.[86]

### *4.4.1. Performance Evaluation of PEC Redox Reactions*

The basic experimental setup of a PEC experiment can take a two-electrode or a three-electrode configuration. Of the electrodes, at least one is photoactive. A key convenience by PEC is the opportunity to separate the photoanode and the photocathode by a membrane. As a result of the separation, the photoelectrocatalyzed oxidation and reduction products can be collected separately. The separation minimizes, if not eliminates completely, the product crossover and hence greatly improves the efficiency. The separation also offers an opportunity to study the two half reactions separately. In practice, the reactions are carried out in either a two-electrode or a three-electrode configuration, depending on whether a reference electrode is employed.[87] For the former, the potentials of the anode would be measured against the cathode. Although this configuration more closely mimics a realistic PEC device in real applications, the inaccuracies of measuring the potential difference between the working and counter electrodes due to, for example, electrolyte polarization, membrane polarization, concentration gradient, among other factors, presents significant challenges in quantitative data analysis. The latter case eliminates these complications with a calibrated reference electrode. In data representations, the photocurrent density-potential (*J*–*E*) curve is most frequently employed to describe a PEC system. Two variables in a *J*–*E* curve, the photocurrent density ($J_{ph}$) and the onset potential ($E_{on}$) are of critical importance (**Figure 9**a).[88] The photocurrent density measures the rate at which the reactions take place, and the onset potential describes the inherent driving force of the reaction. Using water splitting as an example, we show in Figure 9a how these two variables can be utilized to evaluate the performance of a PEC system. Simply, the goal of any integrated PEC system is to obtain a high photocurrent density at the point where the *J*–*E* curve of the photoanode intercepts that of the photocathode ($J_{op}$).[88,89] In order for this to happen, we need the $E_{on}$ of the photoanode as negative as possible, and that of the photocathode as positive as possible. In the case where the $E_{on}$ of the photocathode is less positive than that of the photoanode, external bias would be needed for the overall reaction to take place. For the situation shown in Figure 9a, if we assume 100% Faradic efficiency for both reactions, the solar-to-hydrogen (STH) conversion efficiency ($\eta_{STH}$) can be conveniently calculated as follows:

$$\eta_{STH} = \frac{J_{op} \times (1.23V)}{P_{in}} \tag{3}$$

where $P_{in}$ is the power of overall photon input (W cm$^{-2}$).[88] It is noted that how to correctly calculate the efficiencies of an artificial photosynthesis system has been reviewed by other authors, although no consensus has been reached regarding what is acceptable and what is not.[90]

The utilization of the *J*–*E* curves to describe a PEC is so convenient that it has been overwhelmingly borrowed by most studies aimed at understanding and improving the performance of the photoelectrodes. When treated as being generated by an equivalent circuit of electronic components, the data can be analyzed in a similar fashion to how one would analyze an electronic circuit. It thus opens up opportunities to use alternating current method to interrogate the system for information difficult to obtain by simple direct current methods. For example, various electrochemical impedance spectroscopy (EIS) techniques have been developed to study the system, similar to how EIS was used to study other electrochemical systems.[91] In particular, we wish to mention that photoelectrochemical impedance spectroscopy (PEIS) studies have been carried out by Peter, Bisquert and Hamann et al., separately, to understand the behaviors of the photoelectrode and the co-catalysts.[86g,92] More on this point will be discussed in the following sections. Another useful technique was the intensity-modulated photocurrent spectroscopy (IMPS) pioneered by Peter et al. to characterize the kinetics of the photoelectrodes in a quantitative fashion.[86e] Under ideal conditions, the rate constants of surface recombination, charge transfer can be obtained quantitatively.

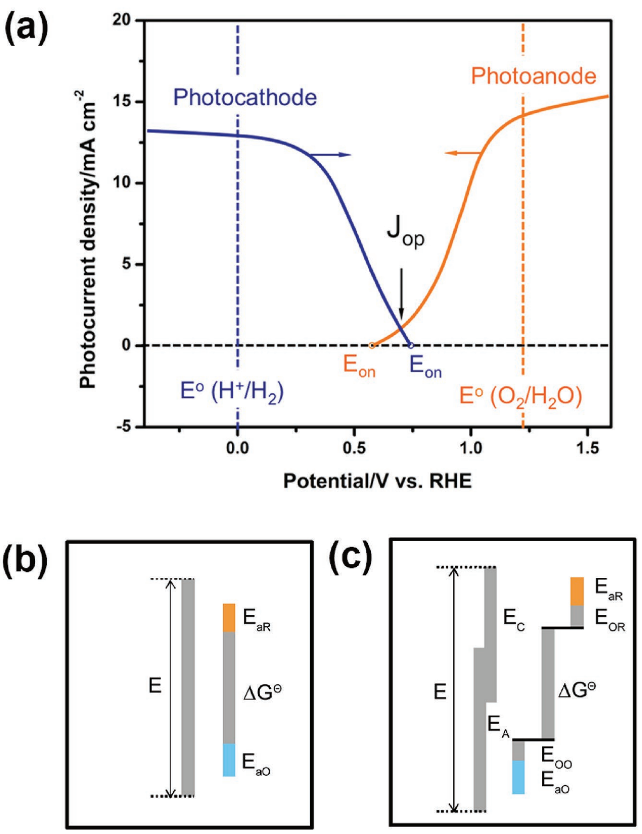


**Figure 9.** a) Overlaid *J*–*E* curves of photoanode (orange line) and photocathode (blue line) in a PEC system. Illustration of energy requirements in photocatalysis b) and photoelectrocatalysis c).

### 4.5. Energy Requirements in Artificial Photosynthesis

The representations of the *J*–*E* curves as shown in Figure 9a provide a good platform to discuss the energy requirements in photocatalytic and/or PEC reactions. In a photocatalytic reaction, to power the overall reactions, one would need a total energy (i.e., the difference between the hole energy level and the electron energy level) no less than the sum of the standard free energies of the reaction ($\Delta G^{\ominus}$) and the activation energies

($E_a$) of the oxidation and the reduction reactions (Figure 9b). That is,

$$E \geq \Delta G^{\ominus} + E_{aR} + E_{aO} \tag{4}$$

Similarly, in PEC, the total solar to chemical energy conversion requires the photoelectrode energy (i.e., the difference between the hole energy level in the photoanode and the electron energy level in the photocathode) no less than the sum of $\Delta G^{\ominus}$, the ohmic loss ($E_O$), and the reaction activation energy ($E_a$) in anode and cathode,[93] expressed as follows (Figure 9c),

$$E \geq \Delta G^{\ominus} + E_{aR} + E_{aO} + E_{OR} + E_{OO} \tag{5}$$

The understanding leads us back to the discussions on the optimum number of light absorbers (Section 2.4). For simplicity, it would be beneficial to have a single light absorber that provides the needed total energy (see, for instance, Figure 9b). As far as water splitting is concerned, it means that the bandgap of the light absorber needs to be >1.6 eV.[94] A more practical value would be 2.0 eV given that reasonable reaction rates are needed, which would add additional kinetic overpotential requirements.[89b] Such a wide gap light absorber is only capable of harvesting the UV portion of the solar spectrum. Even with perfect quantum efficiency (100%), the overall solar-to-chemical energy conversion efficiency would be low. Because of this consideration, we see that having multiple light absorbers as shown in Figure 9c is more beneficial, where a narrow band gap light absorber can be combined with a relatively wide band gap one, to provide the overall energy needs while covering the solar spectrum more broadly than any single light absorber can do.

## 5. Surface Chemistry of Photocatalysts

When photocatalysts in solution are illuminated, photogenerated charges may transfer across the solid/electrolyte interface to promote chemical reactions. They may also recombine within the body and/or on the surface of the photocatalysts. As is true in most heterogeneous catalysis, the catalyst/reactant interface is of paramount importance.[95] The continuous supply of reactants to the photocatalysts, the diffusion of the products away from the reaction sites, and the regeneration of the photocatalysts are all important considerations to ensure the successful functionality of the system (shown in **Figure 10**). In recognition of this aspect, we next examine the photocatalyst/electrolyte interface. Our goal is to understand the chemistry nature of this interface and provide insight into how to optimize the photocatalyst for more efficient photocatalysis.

### 5.1. Interactions with Water

To date most photocatalytic reactions are conducted in aqueous solutions. The interactions between the photocatalysts and water play important roles in different photocatalytic reactions, such as water splitting, pollutant degradation, and $CO_2$ reduction. For instance, as the most studied photocatalyst, $TiO_2$ has been extensively investigated on its water oxidation mechanisms.[96] To date, two water oxidation mechanisms on rutile $TiO_2$ have been discussed, namely the nucleophilic attack (NA) mechanism and the redox photooxidation (RP) mechanism. In the NA mechanism, photogenerated holes are trapped by triply coordinated oxygen on the surface. Some of them diffuse to the bridging O at step, kink, or terrace sites. Water oxidation is considered to initiate from NA by a water molecule (Lewis base) to a surface trapped hole (Lewis acid) at the bridging O, followed by Ti—O bond breaking to form Ti—O·HO—Ti (**Figure 11**a).[96a] The RP mechanism is proposed to initiate water oxidation by interfacial transfer of photogenerated holes to $H_2O_{ads}$, resulting in the formation of $OH_{ads}\cdot$ radicals (Figure 11b).[96c] Although different at the molecular level, the two mechanisms share several important common features. First, water oxidation is initiated at the bridging oxygen site to form surface bound hydroxyl species (Ti—OH·, or Ti—O·HO—Ti). Second, they both involve the formation of surface-bound peroxide species. Third, proton is coupled to electron transfer to play key roles in water oxidation, especially in pH < 13 conditions. More on this point will be discussed next. There is another phenomenon caused by this unique interaction of $TiO_2$ with water under light irradiation, the photoinduced hydrophilicity, which is most often attributed to the structural change of the $TiO_2$ surface under light.[97] Although it is proposed that the photoinduced hydrophilicity may be a consequence of photocatalytic decomposition of surface contaminants, surface decomposition should not be the only cause of photoinduced hydrophilicity since complete decomposition of contaminants has been reported to not necessarily lead to photoinduced hydrophilicity.[97a] Further supporting this conjecture is that photoinduced hydrophilicity can also be achieved when the surface contaminants are still present.[98] From these discussions we see that researches on water oxidation and photoinduced hydrophilicity should benefit from these previous surface studies of $TiO_2$.

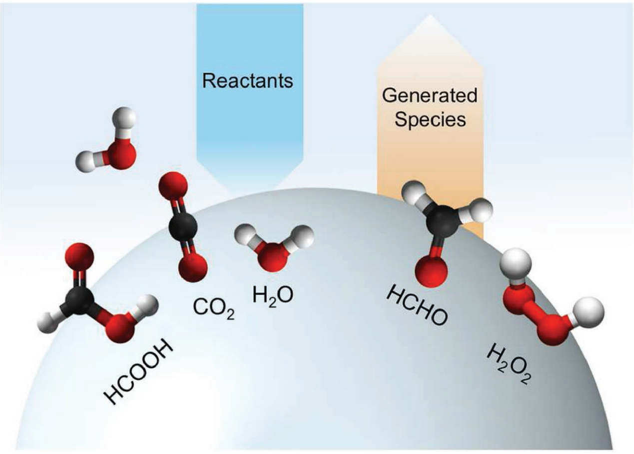
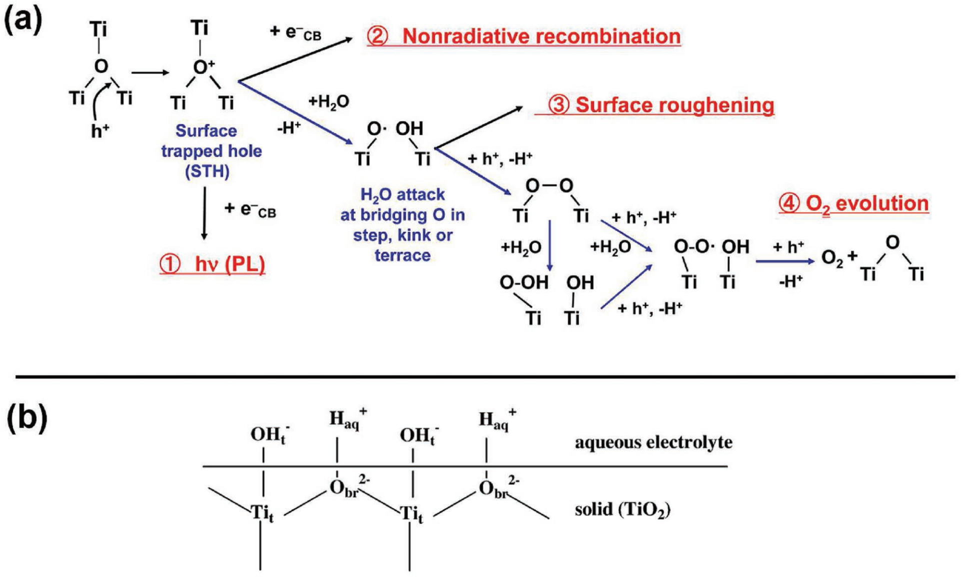


**Figure 10.** Illustration showing surface of photocatalyst.

In parallel, the interactions between hematite ($\alpha$-$Fe_2O_3$) and water have received significant attention. Peter et al. investigated PEC water oxidation by hematite.[99] It was revealed that surface holes accumulate in the form of oxidized surface state. The oxidized surface state was later ascribed to high valence Fe = O species.[100] Zhao and co-workers investigated the key



$$>OH_{br}^{-} + h^{+} \rightarrow -OH_{br}\cdot + H^{+}$$

$$2(-OH_{br}\cdot) \rightarrow >(H_2O_2)_{ads}$$

$$>(H_2O_2)_{ads} + 2h^{+} \rightarrow O_2 + 2H^{+} + 2V[>OH_{br}^{-}]$$

$$2V[>OH_{br}^{-}] + 2H_2O \rightarrow >OH_{br}^{-} + 4H^{+}$$

**Figure 11.** a) Schematic representation of the NA mechanism. Reproduced with permission.[96a] Copyright 2014, American Chemical Society. b) Schematic representation of the RP mechanism. Adapted with permission.[93b] Copyright 2011, Elsevier.

role of protons in water oxidation on hematite surface.[101] The large H/D kinetic isotope effect (KIE) values suggested that electron transfer from water to the oxidized surface state was accompanied by proton transfer to solvent water along the hydrogen bond at pH < 12 (**Figure 12**). That is, water oxidation proceeded according to a concerted proton-electron transfer mechanism during the interfacial hole transfer process. It was highlighted that the addition of buffer plays an important role in tuning the interfacial proton transfer to improve water splitting performance of hematite. Recently, Hamann group reported a detailed study by operando PEC infrared measurements.[102] Their results showed direct evidence of the formation of $Fe^{IV} = O$ intermediates produced from the first hole-transfer reaction on hematite surface.

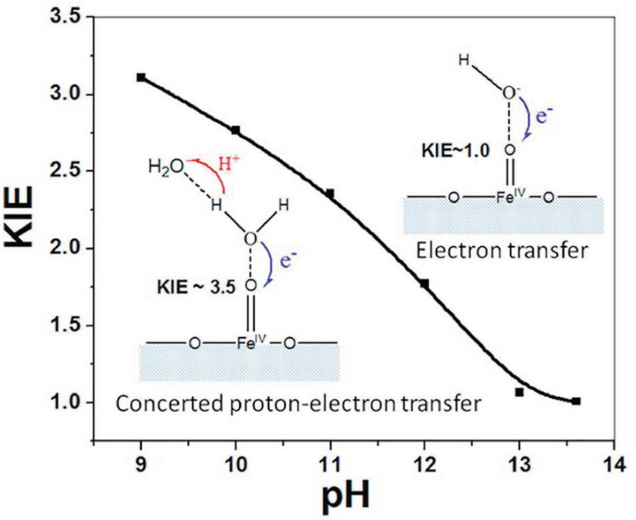


**Figure 12.** KIE values of hematite photoanode in $H_2O$ and $D_2O$ at 1.2 V (vs RHE) at various pH levels and electron-proton transfer mechanisms for oxidation of (left) $H_2O$ and (right) $OH^-$. Reproduced with permission.[101] Copyright 2016, American Chemical Society.

As discussed above, PCET plays important roles in water oxidation in both natural photosynthesis and artificial photosynthesis systems such as $TiO_2$ and hematite surface. Moreover, PCET is also crucial in other photocatalytic redox chemistries. For example, in $CO_2$ photoreduction, the negative potential of the first electron transfer from $CO_2$ to $CO_2^-$ ($E^0 = -1.90$ V vs NHE) makes the reduction of $CO_2$ thermodynamically unfavorable.[103] The presence of protons together with $CO_2$ on the surface of photocatalyst was found to lead to multiple proton-coupled electron transfer processes with significantly reduced potential requirement to bypass the formation of $CO_2^-$. The role of protons in $CO_2$ photoreduction was investigated by experiments and theoretical calculations.[104] As shown in **Figure 13**, the initial stage was competitive electrons transfer from $TiO_2$ to $CO_2$ and protons. The process resulted in the breaking of O=C=O bound and the attachment of a H atom to form $HCOO^-$. The overall process corresponded to a two-electron, one-proton transfer process. The following consecutive electron/proton transfer led to the formation of methoxyl radicals, which were directly detected by EPR.[104] The PCET process at the initial stage further supports the critical role of protons in $CO_2$ photoreduction.

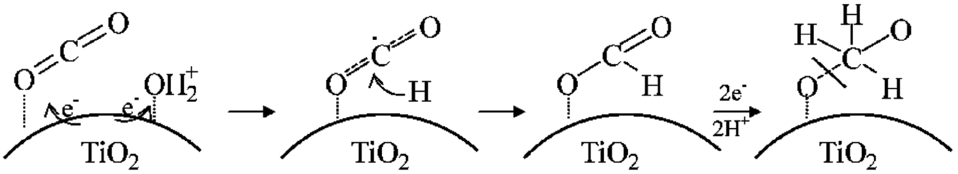


**Figure 13.** Mechanism of photoreduction of $CO_2$ to methoxyl radical on $TiO_2$ in the presence of water. Reproduced with permission.[104] Copyright 2011, American Chemical Society.

### 5.2. Interactions with Reactants

For organic molecule/gas reactants related reactions, it is of great importance to understand the reactant adsorption on the surface of the photocatalyst. The surface interaction plays a crucial role in the photocatalysis mechanism. It was discovered that different interactions of $TiO_2$ with formic acid, benzene, and phenol resulted in different oxidation mechanisms of these molecules.[105] For instance, formic acid strongly chemisorbed on $TiO_2$ in water (**Figure 14**a), resulting in direct photo oxidation by trapping photogenerated valence band holes, hence the direct transfer (DT) mechanism. In contrast, chemisorption of benzene on $TiO_2$ surface in acetonitrile was not favored. Physisorbed benzene on $TiO_2$ was observed to be photooxidized via an indirect transfer (IT) mechanism by the photogenerated terminal $-O^{s-}$ radicals (Figure 14b). For phenol, it could both chemisorb and physisorb on $TiO_2$ (Figure 14c,d). Its photooxidation mechanism was found to depend on the solvent used. When dissolved in water, phenol was photocatalytically oxidized via a direct-indirect mechanism. The IT photocatalytic oxidation mechanism led to reaction rates one order of magnitude higher than that by the DT mechanism. The difference was due to the competition between water and phenol in binding with $TiO_2$ adsorption sites. When $H_2O$ was replaced by acetonitrile, the reaction rates due to the IT mechanism remained unchanged. The reaction rates due to the DT mechanism, on the other hand, were increased by 2 orders of magnitude because the interaction between the solvent (acetonitrile) and $TiO_2$ was now negligible.

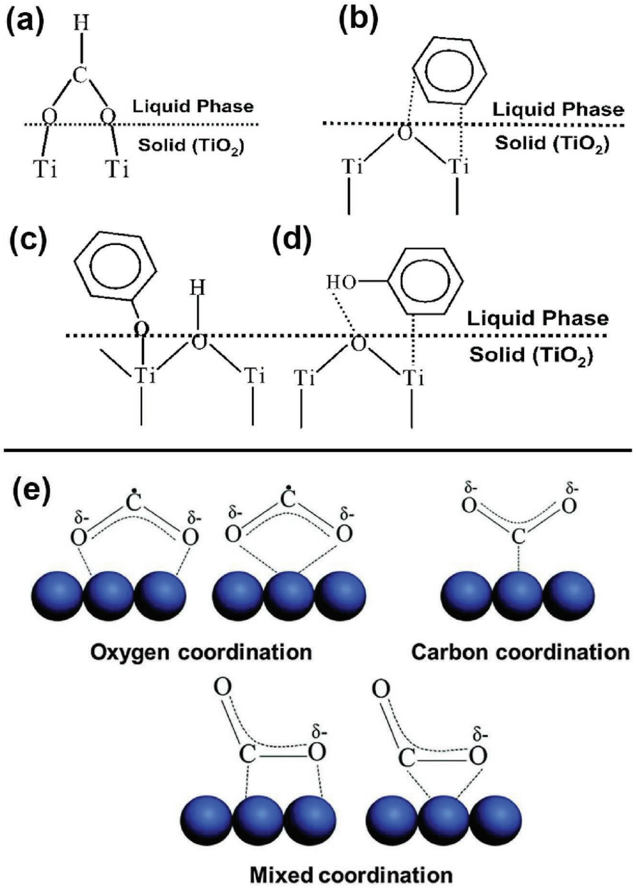


**Figure 14.** a–d) Interaction modes of different reactants on $TiO_2$: formic acid chemisorption (a), benzene physisorption (b), phenol chemisorption (c), and phenol physisorption (d). Solid line: covalent bonding; dashed line: weak interactions such as Van der Waals forces. Reproduced with permission.[105] Copyright 2014, American Chemical Society. e) The three possible structures of partially charged $CO_2^{\delta-}$ adsorbed on catalysts. Reproduced with permission.[107a] Copyright 2016, The Royal Society of Chemistry. Reproduced with permission.[107b] Copyright 2006, Elsevier.

In photocatalytic reactions involving gaseous reactants, it is critical to adsorb the gas molecules onto the photocatalyst surface to promote favorable redox reactions and to suppress the competing ones. For instance, in photocatalytic $CO_2$ reduction, the difficulty to adsorb gaseous $CO_2$ reactants to the photocatalysts and the thermodynamically unfavorable one-electron reduction of $CO_2$ result in a generally low yield of products. Liu et al. proposed five adsorption modes to investigate the interaction between $CO_2$ molecules and the surface of $Zn_2GeO_4$ using density functional theory (DFT).[106] It was found that different facets of the photocatalyst favor different $CO_2$-adsorbed structures, depending on the adsorption energy in each mode. It was proposed that $CO_2$ chemisorbed on catalysts with three structures (Figure 14e): (1) oxygen coordination structure with oxygen donating electrons to surface Lewis acid centers; (2) Carbon coordination structure with carbon gaining electrons from Lewis base centers; (3) Mixed coordination structure with carbon gaining electrons and oxygen donating electrons.[107] The chemisorption of $CO_2^{\delta-}$ changed $CO_2$ geometry from linear structure to a bent form, which featured a lower barrier for accepting an electron since the LUMO level decreased as the molecule bended.

Researchers have studied how to promote chemisorption of $CO_2$ through surface active sites such as active metal Cu and oxygen vacancies.[108] It was reported that Cu acted as an active site for $CO_2$ adsorption, thus enhancing the photocatalytic $CO_2$ reduction efficiency.[108a] In situ FTIR (Fourier transform infrared spectroscopy) spectra of Cu-added MOF photocatalyst with asymmetric stretching vibration $\nu_{as}$(OCO) of the "end-on" and "C-coordination" coordination states supported the chemisorption of $CO_2$, whereas no $CO_2$ signal was observed on MOF photocatalyst without Cu. $CO_2$ adsorbed on the surface of $SrTiO_3$ was also studied, where $Ti^{4+}$ ions in $SrTiO_3$ were substituted by other metal ions with smaller electronegativity.[109] $SrTiO_3$ doped with Co ions showed enhanced $CO_2$ adsorption and photocatalytic $CO_2$ reduction activity. At the same time, it was widely reported that surface states such as oxygen vacancies on the surface of photocatalysts might act as $CO_2$ adsorption active sites, leading to enhanced photocatalytic activity for $CO_2$ reduction.[108b]

### 5.3. Interactions with Photogenerated Species

In a typical photocatalytic reaction, the relative binding strength of the reactants, intermediates, and products to the photocatalyst surface is of critical importance. For example, Guo et al. investigated the photocatalytic dissociation of partially deuterated methanol ($CD_3OH$) and water on $TiO_2$ (110).[110] It was found that the dissociation of $CD_3OH$ began with O–H dissociation first and then followed by C–D dissociation to finally form $CD_2O$. Two factors were important to the successful dissociation of $CD_3OH$ to $CD_2O$. The first factor was the high barrier for the D atom to jump back to the adsorbed $CD_2O$. The second factor was the easy desorption of $CD_2O$ product from on $TiO_2$ (110) surface. This body of research supports that facile desorption of photocatalytic products helps promote forward reactions. Another example concerns the study of $WO_3$. It was widely reported that bare $WO_3$ exhibited poor PEC water oxidation stability.[111] Lewis et al. revealed that the photocurrent decrease of $WO_3$ in $HClO_4$ was due to the binding of photogenerated $ClO_4\cdot$ on $WO_3$, which blocked the active site for water oxidation.[111b] More recently, graphitic-$C_3N_4$ (g-$C_3N_4$) receives significant attention owing to its excellent water reduction activity for hydrogen evolution.[112] However, when used for full water splitting, g-$C_3N_4$ exhibits poor activity due to the poisoning effect by photogenerated $H_2O_2$ on g-$C_3N_4$.[113] It was found that when co-catalysts that can promote $H_2O_2$ decomposition are present, the performance of overall water splitting by g-$C_3N_4$ is greatly improved.[113] These results highlight the importance of the interactions between photocatalyst and adsorbates in photocatalysis.

## 6. Integrated Photocatalyst System

In a simplistic view, a good photocatalyst should meet at least three requirements simultaneously, namely efficient light absorption (ideally in the visible range), high photocatalytic activity, and good stability against photocorrosion. These considerations often lead to complex, sometimes conflicting, property expectations from the photocatalysts. For instance, to drive redox reactions, we desire large enough bandgaps. But the bandgap should also be small enough so as to absorb broadly in the solar spectrum. Similarly, for high photocatalytic activities, we desire highly active surfaces, which would mean less stability against photocorrosion. How to minimize charge and product recombination on the surface of the photocatalyst in contact with a solution is not a trivial task either. These considerations underscore why it has been exceedingly difficult to find a single material that can satisfy all the above-listed requirements at the same time. Realistically, most successful photocatalysts studied to date feature wide bandgaps so they are inherently low efficiency.[114] Many of them show fast charge recombination in the bulk and/or on the surface. Combined with slow surface charge transfer kinetics, these photocatalysts can only deliver a small portion of the photogenerated charges for desired chemical conversion. In the meanwhile, poor long-term stability caused by self-degradation is another serious issue that limits further development of photocatalysts for large scale, long-term commercial implementations.[115] To address these issues, researchers have exploited the idea of combining different components, each specifically designed to meet one or two aspects of the considerations, for the achievement of the overall properties.[116] For example, additional light absorbers, co-catalysts, and/or protection layers have all been studied.[117] Increasingly, we see that the integrated system resembles that of the natural photosynthesis machinery (**Figure 15**).

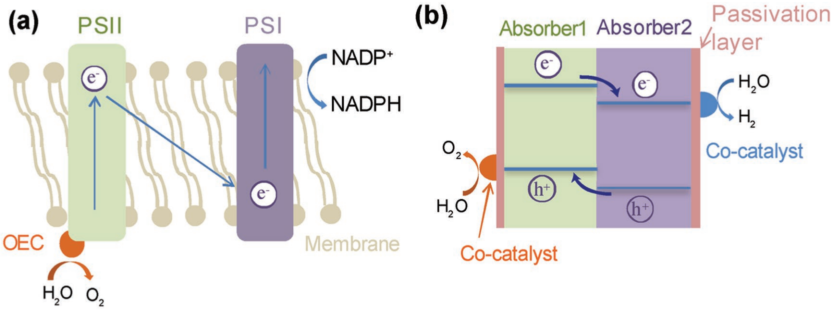


**Figure 15.** Illustration showing natural photosynthesis system: a) and artificial integrated photocatalyst system, b) light absorber combined with additional light absorber, co-catalyst, and passivation layer.

### 6.1. Forms and Effects of Integrated Systems

#### *6.1.1. Combination with Additional Semiconductors*

While the materials for individual redox reactions, e.g., water oxidation, water reduction, and $CO_2$ reduction, are numerous, those that can power the overall reactions involving both oxidation and reduction are rare, let alone examples that are efficient for the overall process under visible light illumination. The idea of combining two (or more) light absorbers offers an opportunity to break this barrier by offering high enough photovoltages (Figure 9b,c) by absorbing complementary regions of the solar spectrum. The gradient of the internal potentials generated by different absorbers create a driving force to guide the one-way charge flow within the integrated system, similar to how charges are separated in the natural photosystem. Below, we examine various strategies falling in these considerations in more details.

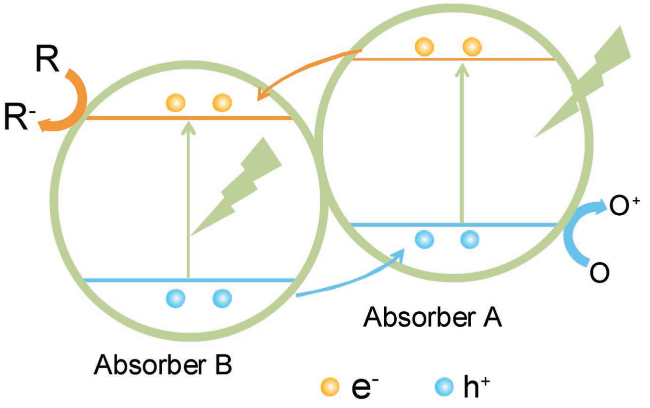


**Figure 16.** Illustration of charge separation in a favored heterojunction. R: chemicals in reductive reactions, O: chemicals in oxidative reactions.

*Wider light absorption by multiple absorbers*: The idea is to couple a narrow bandgap semiconductor (or a visible-light absorbing molecular photocatalyst) with a wide bandgap host semiconductor. While it can be the other way around, more often we see that a small bandgap light absorber is added to a wide bandgap photocatalyst. This way, photons in the short wavelength region of the solar spectrum are absorbed by the main photocatalyst, and those of lower energies can be taken advantage of by the narrow bandgap co-absorbers. Examples of this design can be found in $TiO_2$-based systems, where small bandgap materials such as CdSe (1.7 eV for bulk, 2.4 eV for quantum dot) have been introduced for the absorption of visible light.[118] Another example is the combination of $TiO_2$ with PdS.[119]

*Better charge separation*: The direct contact between two light absorbers results in the formation of a heterojunction. Using two-semiconductor photocatalysts as an example, we illustrate an optimized band diagram of such a heterojunction in **Figure 16**. Electrons in the CB of semiconductor A are driven to the CB of semiconductor B and holes from the VB of semiconductor B to that of semiconductor A, driven by an internal built-in field. The net result is the separation of photogenerated charge facilitated by the heterojunction.[120]

*Greater photovoltages*: As discussed in Section 4.5, to drive the overall reactions, the total input energy should be no less than the sum of the changes of the standard free energies and activation energies of both the oxidation and the reduction reactions. Consider PEC water splitting as an example. A single semiconductor with a bandgap of 1.6–2.0 eV could in principle enable the overall reaction.[89b,94] However, due to the low photovoltage (as limited by the difference between the flatband potential of the semiconductor and the electrochemical potential of the desired reactions) and the less-than-ideal band edge positions, a significant external bias potential is necessary.[121] Previous research by us has shown that the situation can be greatly improved by depositing a thin layer of an additional semiconductor to form a buried junction.[86] We studied the effect of a thin layer of n-type ZnS on p-type $Cu_2O$ and confirmed the increase of band bending of $Cu_2O$. The photovoltage was increased correspondingly from 0.60 V to 0.72 V, as evidenced by the positive shift of the open circuit potential under light irradiation (**Figure 17**).

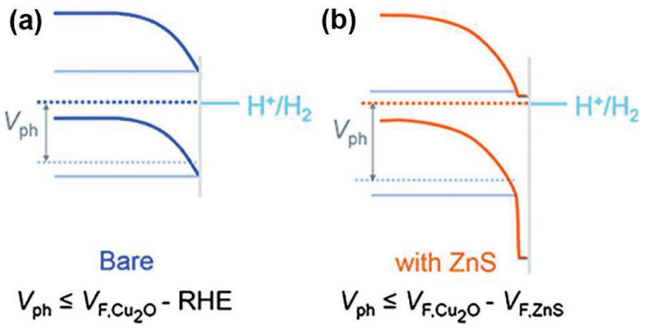


**Figure 17.** Energy band diagram of $Cu_2O$ a) and $Cu_2O$/ZnS b). The band edge positions of $Cu_2O$ are shown in pale blue solid line and the Fermi level of $Cu_2O$ is in pale blue short-dashed line. Reproduced with permission.[86] Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

*Separation of incompatible redox reactions*: As shown in Figure 16, a combined photocatalyst involving two separate light absorbers makes it possible to guide photogenerated holes and electrons to different directions. This opens up opportunities to separate incompatible redox reactions. By contrast, the close vicinity of the reduction and oxidation sites on a nanoscale photocatalyst increases the chances of product crossover and recombination. Consequently, the overall efficiency is reduced. Such an issue can be circumvented by an integrated system as shown in Figure 16. In a way, the integrated photocatalyst can be regarded as a micro-PEC cell with well separated photo oxidative and photo reductive sites. A derivative of the design is to avoid direct contact of the two light absorbers, in which case a mediator would be needed to facilitate charge transfer between the light absorbers. Importantly, the mediator can be a solid or a redox couple in the solution.[122] Again, we wish to draw the connections between the improved design with the Z-scheme in the natural photosystem.

### 6.1.2. Combination with Co-Catalyst

Highly active electrocatalysts as co-catalysts have been popularly explored as a means to reduce overpotential requirement so as to reduce the overall photovoltage requirements from the light absorbers.[88] Another way to think about the benefit of co-catalysts is that they facilitate forward charge transfer and thus reduce charge recombination. Nevertheless, the integration of co-catalyst introduces new solid/solid interfaces between the light absorber and the co-catalyst, resulting in complications that only start to receive due attention.[123] Below, we summarize some of the key roles played by co-catalysts within the photocatalytic context.

*Lower activation energies*: The primary motivation of integrating co-catalysts is to exploit their efficient catalytic properties in much the same way as how they are being used in electrocatalysis. The presence of co-catalysts on a light absorber is supposed to provide active sites with lower activation energies for surface reactions. For example, Pt is known for its relatively low activation energies for $H_2$ evolution.[124] The integration of a semiconducting light absorber with Pt has been shown to greatly facilitate photocatalytic hydrogen evolution.[125]

*Better charge separation*: Co-catalysts affect charge separation in the light absorber in several different ways. For example, noble metals such as Ag,[126] Pt,[127] and Pd[128] have been studied and shown to reduce the possibility of electron-hole recombination by serving as an electron sink. In other words, upon illumination, these metals provide favorable sites for electrons to concentrate, thereby better separating electrons from holes. For another example, some metal oxides as water oxidation catalysts can facilitate charge separation by decreasing charge recombination when combined with light absorbers.[86b,129] In the meanwhile, direct contact between co-catalysts and a light absorber creates new interfaces. The nature of these interfaces plays an important role in defining the charge separation capability.[130] For instance, $MoS_2$/CdS with intimate junctions exhibited better photocatalytic hydrogen evolution performance than Pt/CdS, even though Pt was known to feature superior catalytic activity toward electrocatalytic HER than $MoS_2$.[131] Another example is the surface energetics change of hematite/co-catalyst compared to bare hematite photoanode. Due to Fermi level pinning caused by "surface states", the degree of band bending did not change with the increase of applied voltage, meaning that the increased voltage did not help to achieve better charge separation.[86h] We deposited $NiFeO_x$ co-catalyst on hematite and carried out energetic measurements of hematite with and without $NiFeO_x$ co-catalyst.[86a–c] The existence of $NiFeO_x$ on hematite could alter surface energetics by removing surface states. These results indicated that with the help of $NiFeO_x$ the band bending of hematite increased compared with bare hematite, leading to better charge separation. The results highlighted the crucial effect of designing and controlling the interface for optimized charge transport in an integrated photocatalyst system.

*Improved stability*: In many cases, photocatalysts suffer from activity degradation due to self-oxidation/reduction caused by accumulated holes/electrons. The deposition of co-catalysts on the light absorber surface protects the photocatalyst from self-decomposition by effectively removing holes/electrons from the light absorber. As a result, photostability is effectively enhanced. Note that such a protection is fundamentally different from passivation which relies on retarding surface chemical reactions. More on this point will be discussed in the next section. A good example of this effect can be found in a recent study by Li et al. where the authors developed ferrihydrite co-catalysts as "holes storage layer".[132] They reported that this layer suppressed hole-induced self-oxidation of $Ta_3N_5$ and improved the stability of $Ta_3N_5$ by a large margin. Another mechanism by which photocurrents can decay is the accumulation of products/by-products/intermediates on the surface of the photocatalyst, blocking the active sites for continuous reactions. Co-catalysts that can help decompose these species will improve the stability effectively. In this category, carbon nanodots have been recently shown to enhance the g-$C_3N_4$ photocatalytic water splitting stability by decomposing hydrogen peroxide, which is the oxidation product of water by g-$C_3N_4$.[113] The surface accumulation of $H_2O_2$ is recognized as the key reason for the quick decay of g-$C_3N_4$'s performance in overall water splitting.[113]

*Broader light absorption*: Apart from the above mentioned advantages, another unique positive consequence of the integrated light absorber/co-catalyst system is to enhance the photocatalytic efficiency by the plasmonic effect. Briefly, a plasmonic metal harvests the photon energy through localized surface plasmon resonance oscillations.[133] The energy can then be transferred to the photocatalyst through at least three different mechanisms, direct electron transfer,[134] plasmon induced resonant energy transfer,[135] and local electromagnetic field enhancement.[136] Interested readers are suggested to read several recent reviews on this topic.[137] We list this category here because many of these plasmonic materials are also known co-catalysts, such as metals including Au,[138] Ag,[139] Pd,[140] Cu,[141] Al,[142] and non-metals including $Cu_{2-x}Se$,[143] $Cu_{2-x}S$,[144] $WO_{3-x}$[145] and each of them features unique resonant photon wavelengths. Importantly, the resonant photon wavelength of the plasmonic nanoparticles can be tuned by varying their sizes, shapes, and material compositions. It provides a versatile route to photocatalyst design for better utilization of the entire solar spectrum.

#### *6.1.3. Combination with Surface Passivation Layer*

While in general stability is of paramount importance to catalysis, this is particularly true for photocatalysis because the inclusion of light facilitates the formation of energetic intermediates that can easily corrode the photocatalysts. As discussed above, the degradation of photocatalytic performance is mainly due to chemical corrosion by surface accumulated species such as high concentration of $OH^-$ and self oxidation/reduction caused by photogenerated holes/electrons. The idea of introducing surface passivation layer is to isolate the light absorber from these reactive species, so as to avoid direct photocatalytic reactions on the light absorber surfaces. In a way, this can be regarded as a brute force stabilization strategy, which has proven effective for improving the stability of a large number of systems. Some added benefits of the passivation layer include reduced surface recombination by removing surface recombination centers. Consequently, the overall charge separation within the photocatalyst is also improved. For example, recent work by us revealed that the surface oxidation of $Ta_3N_5$ during PEC water oxidation results in a thin layer of oxynitrdie (<3 nm).[146] Although thin, this layer almost completely suppressed the photoactivity of $Ta_3N_5$. MgO was shown effective as a barrier to separate $Ta_3N_5$ from $H_2O$ and, hence, reactive O species. Such a protection layer led to significantly better stability as well as improved fill factors, supporting that better charge collection was enabled by reduced surface recombination. In another investigation, researchers quantitatively evaluated the surface recombination of ZnO and ZnO/$TiO_2$ via in situ spectroscopic methods.[147] It was revealed that 37% of the IPCE (incident photon-to-current efficiency) was lost through bulk and surface recombination in ZnO. A thin layer $TiO_2$ on ZnO reduced the surface recombination by 14% and enhanced the photocatalytic efficiency.

### 6.2. Challenges Presented by Integrated Photocatalyst Systems

There remain challenges towards efficient enough photo activity in the integrated systems. Some of the issues are listed below.

### *6.2.1. Blocking Active Site*

When a light absorber is combined with an additional semiconductor/co-catalyst/passivation layer, some of the inherently active sites on the light absorber would be blocked by the guest materials. This is particularly true when the coverage of the guest materials is excessive. For example, Bai et al. designed two different phases of $MoS_2$: $MoS_2$(1T) and $MoS_2$(2H) to integrate with $TiO_2$.[148] $TiO_2$-$MoS_2$(1T) showed enhanced photocatalytic properties, whereas $TiO_2$-$MoS_2$(2H) exhibited lower photocatalytic performance than bare $TiO_2$. The difference was attributed to the blocking of active sites on the surface of $TiO_2$ by $MoS_2$(2H) that are not active. In another example, Ag/$BiVO_4$ with 4 wt% Ag loading showed decreased photocatalytic activity than those with lower Ag loading.[149]

### *6.2.2. Shielding Light Absorption*

The second challenge of integrated photocatalyst is decreased light absorption due to the shielding effect caused by the guest materials. Many experimental studies demonstrated that when combined with materials such as carbon nanotubes,[150] graphene,[151] and $NiS_x$,[152] the composite materials showed lower light absorbance. In recent years, researchers have started to develop optically transparent guest materials, in the hope to minimize undesired light shielding. A number of optically transparent co-catalysts have been reported, including $Co(OH)_2/Co_3O_4$,[86g] $NiO_x$,[153] and $NiFeO_x$.[154] These optically transparent materials have proven promising guest materials for photocatalysis.

### *6.2.3. Mismatch Between Light Absorbers and Guest Materials*

As is true in most junctions, the introduction of additional material components increases the chances of recombination for a number of reasons. Aside from structural defects, the energetics of the interface need to be carefully engineered to minimize mismatches, which could set up charge traps for significant recombination. For instance, when $Fe_2O_3$ was combined with $TiO_2$, the conduction band minimum and valence band maximum of the latter straddle those of $Fe_2O_3$, meaning that photogenerated electrons and holes promptly transfer to $Fe_2O_3$ from $TiO_2$.[155] The net result is that little benefit was gained by having $TiO_2$ in this system. In another work, it was revealed that photoactive $Cu_2O$ octahedras became inactive after the deposition of ZnO.[156] The result was explained by unfavorable band alignment at the interface between ZnO (101) and $Cu_2O$ (111).

## 7. Kinetic Information of Photocatalyst/Co-Catalyst Systems

Recent works in designing composite photocatalysts showed enhanced photocatalysis performance. However, most of the photocatalysis studies focused on the overall photo-to-chemical conversion efficiency. A clear understanding of the detailed processes, particularly those concerning charge transfer, is still lacking. Such knowledge is important because it holds the key to further improvement. In this section, we aim to provide a general account on recent studies designed to fill in this knowledge gap. Two key electrochemical techniques, IMPS and PEIS, are at the heart of our discussions. The goals of these studies are to collect quantitative information on the kinetics of the photocatalytic reactions. Of them, the theory behind IMPS considers the kinetics of two main competing processes, forward charge transfer and backword charge recombination, their rate constants denoted as $k_t$ and $k_r$, respectively (**Figure 18**).[157] The net charge transfer efficiency is then defined as $k_t/(k_t + k_r)$. PEIS considers each part of the photocatalytic process as an electronic element in a combined circuit.[92a] For example, the resistance of charge transfer can be described as a resistor and the capacitive behaviors of an interface may be modeled as a capacitor. Thus, the electronic behavior of the overall reaction can be mathematically modeled by an equivalent circuit, the details of which can be probed by alternating current (AC) techniques developed for the understanding of electronics. The parameters of each electronic element yield quantitative information of the corresponding process(es). A third technique, transient absorption spectroscopy (TAS), has also been employed to study the charge dynamics on time scales between a few picoseconds to milliseconds.[158] For the ease of discussions and to keep in sync with the rest contents of this review, we focus our attention to the semiconducting photocatalyst and co-catalyst combinations.

### 7.1. Kinetics of Photogenerated Electrons

For efficient utilization of photogenerated electrons, noble metals are popularly studied as co-catalysts or plasmonic decorations or both. For instance, it was reported that Au nanoparticles on $TiO_2$ expanded the light absorption through plasmonic effect.[159] Transient absorption kinetic analysis and PEC studies revealed that hot electrons generated by the plasmonic effect

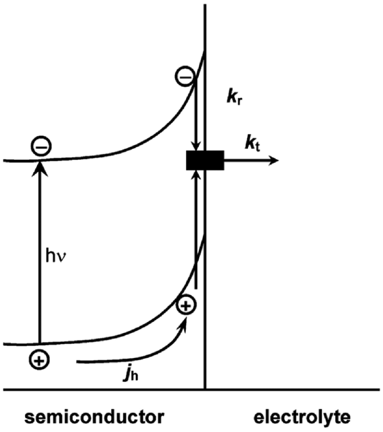


**Figure 18.** Scheme showing competition between charge transfer and surface recombination. $j_h$: hole flux into the surface; $k_t$: first order rate constant of charge transfer; $k_r$: first order rate constant of surface recombination. Reproduced with permission.[157] Copyright 2011, The Royal Society of Chemistry.

transfer from Au directly to the conduction band of $TiO_2$. The lifetimes of these electrons were shown 1–2 orders of magnitude longer than those of the conduction band electrons in $TiO_2$. Nevertheless, the true role of noble metal nanoparticles in such systems remains the subject of debates.[160] For one reason, the reported enhancements due to the plasmonic effect were limited. Furthermore, how the introduction of metal to a semiconducting light absorber influences the nature of the metal-semiconductor junction can be complicated. In a study focused on the $TiO_2$/Ag interface, Kamat et al. investigated the electron behaviors across and found that Ag enhanced the photoelectrochemical performance $TiO_2$ by capturing and storing photogenerated electrons with an apparent negative shift of the Fermi level (**Figure 19**a).[160]

Along this line, these authors also investigated charge transfer behaviors in CdSe/Pt and CdSe/Pt/$MV^{2+}$ systems (Figure 19b).[158a] Transient absorption spectra revealed that the rate of electron transfer from CdSe to Pt nanoparticles was $1.22 \pm 0.19 \times 10^9$ $s^{-1}$. In the CdSe/Pt/$MV^{2+}$ system, both $MV^{2+}$ and Pt were good electron acceptors but they worked in different ways. The electron transfer rate constant from CdSe to $MV^{2+}$ was $1.7 \pm 0.11 \times 10^{10}$ $s^{-1}$, which was faster than electrons transfer to Pt. But the electrons transferred to the surface bounded $MV^{2+}$ were quickly scavenged by Pt as the low-lying Fermi level of Pt made it a good electron acceptor. These results suggest that Pt in this system acts as an electron sink to enhance charge separation.

In addition to metal co-catalysts, molecular co-catalysts have been studied in photocatalyst systems. Different from bare photocatalysts and inorganic co-catalysts, molecular co-catalysts typically require multiple oxidation/reduction steps to enable the desired photocatalytic reactions. In such a system, the electron transfer from semiconductor to co-catalyst can be more complicated. For instance, a cobaloxime $H_2$ evolution catalyst (CoP) covalently attached to $TiO_2$ was revealed to undergo double reduction of CoP from $Co^{III}$ to $Co^{I}$ in order to drive the proton reduction to hydrogen.[161] Transient absorption results suggested that the reduction from $Co^{III}$ to $Co^{II}$ and $Co^{II}$ to $Co^{I}$ were very different. The first reduction step of the co-catalyst by electrons from the semiconducting light absorber could proceed quickly, but the second reduction, which was desired for hydrogen evolution, appeared to be $10^5$ times slower. In other words, the molecular co-catalyst was efficient in extracting photogenerated electrons from the light absorber to complete the first step of reduction, but faced a RDS of the second electron transfer.

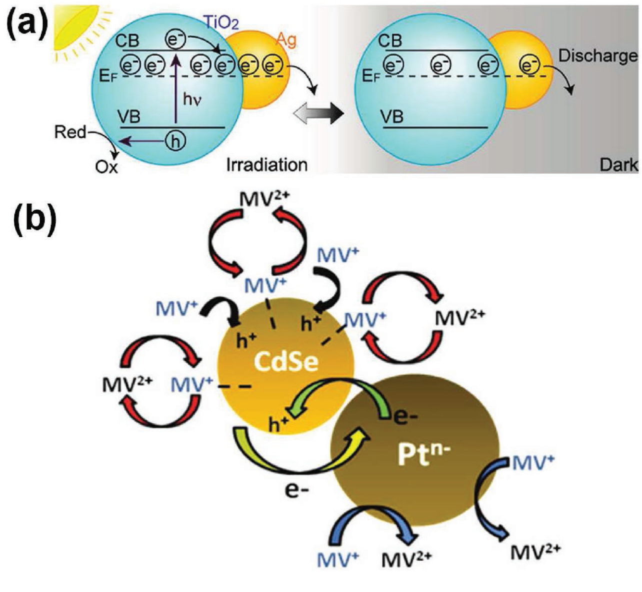


**Figure 19.** a) Scheme showing equilibration between $TiO_2$ and Ag: under UV irradiation (left) and in the dark (right). Reproduced with permission.[160] Copyright 2011, American Chemical Society. b) Scheme showing reactions in the CdSe/Pt/$MV^{2+}$ system. Dashed line: electrostatic interactions; red arrow: charge transfer between $MV^{+}$ and $MV^{2+}$; blue arrow: charge transfer between $MV^{2+}$ and Pt; green arrow: oxidation of $Pt^{n-}$ by holes from CdSe; yellow arrow: direct photogenerated electron transfer to Pt; black arrow: oxidation of $MV^{+}$ radicals by holes from CdSe. Reproduced with permission.[158a] Copyright 2010, American Chemical Society.

## 7.2. Kinetics of Photogenerated Holes

Compared with proton reduction, water oxidation is far more difficult due to its 4-electron, 4-proton nature. It is regarded as the limiting factor in solar water splitting research. As such, the detailed understanding of the kinetics of photogenerated hole transfer in water oxidation reactions is of critical importance. It has indeed received significant attention.

### *7.2.1. Enhanced Charge Transfer*

Despite the obvious reason to introduce water oxidation co-catalysts for faster reaction kinetics, direct evidence that supports mechanisms aligned with this motive is few in the literature. As a rare example that does support this mechanism, hematite photoanode was coated with a thin layer of cobalt oxide catalyst.[86g] The PEC water oxidation performance was significantly enhanced as evidenced by the 100–200 mV cathodic shift of the onset potentials. The authors employed PEIS to investigate the role of the catalyst. Two key features can be seen from the data shown in **Figure 20**. First, the deposition of cobalt oxide catalyst reduced the magnitude of the peak capacitance connected to the surface catalytic reactions. It supported that better charge transfer decreased the need for high surface hole concentration. Second, the potential at which the surface capacitance peaks was cathodically reduced by 100 mV, suggesting that a lower overpotential was obtained. Together, these results prompted the authors to conclude that the cobalt oxide catalyst functioned as a true catalyst by facilitating charge transfer.

### *7.2.2. Reduced Charge Recombination*

In a somewhat interesting twist, there are more reports support that the role of the water oxidation co-catalysts actually improve the performance of the overall reaction by reducing recombination. Peter et al. pioneered kinetic and mechanistic studies on PEC water oxidation by hematite. They suggested that the apparent "catalytic" effect by surface treatments with Co(II) was in fact owing to the suppression of surface recombination but

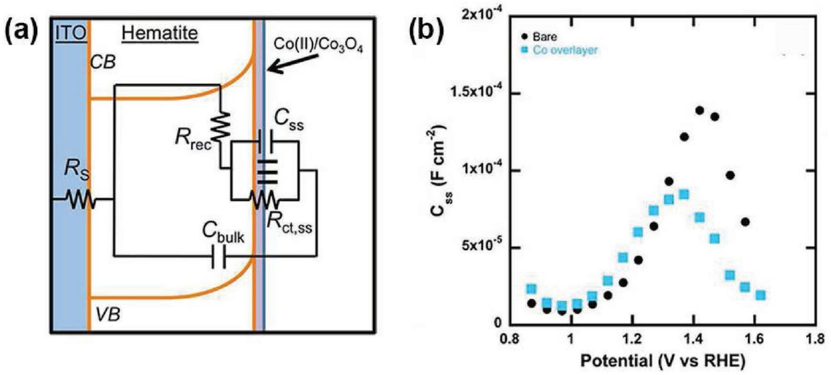


**Figure 20.** a) Equivalent circuit of water oxidation on photoelectrodes. b) Representative $C_{ss}$ for a bare hematite photoanode (black dot symbols) and a hematite deposited with 1 ALD cycle Co(II)/$Co_3O_4$ (blue square symbols). Reproduced with permission.[86g] Copyright 2013, American Chemical Society.

not to the acceleration of charge transfer.[86e] Li et al. reported that $Ni(OH)_2$ "hole storage layer" captured the photogenerated holes from hematite to reduce electron-hole recombination at the interface of hematite and $IrO_x$ catalyst.[86d] In particular, cobalt phosphate (Co-Pi) as water oxidation co-catalyst has received significant attention. Correspondingly, there have been a large number of studies on their mechanisms when combined with photocatalysts. Gamelin et al. were the first to report that the addition of Co-Pi significantly enhanced the performance of hematite.[162] But it was not until recently did the authors show the PEC water-oxidation kinetics actually slowed upon addition of Co-Pi to the $\alpha$-$Fe_2O_3$ surface.[163] What improved the overall performance is the greater suppression of surface electron-hole recombination as compared to charge transfer. As a result, the overall charge transfer efficiency was improved (**Figure 21**).

As far as the mechanism of Co—Pi on hematite is concerned, the works by Barroso et al. are especially notable. They studied the kinetics using transient absorption spectroscopy in the micro to millisecond range.[164] No evidence of faster hole transfer, as expected from shorter hole lifetimes, was observed. Instead, they observed longer lived holes, which the authors attributed to direct evidence of reduced recombination. In other words, the main role of the Co-Pi co-catalyst was to "passivate" the surface of hematite for reduced recombination but not to "catalysze" the surface for faster charge transfer. Later, the same group extended similar studies to a variety of different surface modifications, including $CoO_x$ and $Ga_2O_3$ overlayers.[158b] The last example is particularly worth noting because $Ga_2O_3$ is not known as an active water oxidation catalyst, and yet it improved the performance of water oxidation by hematite, supporting the authors' conjecture as stated above.

On a parallel system, we have embarked on a study of $NiFeO_x$ as a water oxidation co-catalyst. It enabled one of the most notable cathodic shifts in hematite PEC water oxidation performance, up to 400 mV.[86c] To study the true reasons for the dramatic performance improvement, we carried out a series of systematic studies focused on probing the thermodynamic equilibrium potentials and found that the cathodic shift can be fully accounted for by the shifts of the Fermi levels. That is, the performance improvement was entirely due to better charge separation as a direct result of reduced surface recombination. Similar conclusions were drawn on other photoelectrode materials such as $TiO_2$ as well.[86a] The understanding was further cemented by quantitative kinetic measurements by IMPS, where the $k_t$ was shown to remain slow with the introduction of $NiFeO_x$, but the $k_r$ was significantly reduced (>10 times).[86b]

### *7.2.3. Both Reduced Charge Recombination and Enhanced Charge Transfer*

The works by Hamann et al. on the Co-Pi/hematite system provided further insights into the detailed mechanism.[86j] They confirmed that Co in the Co-Pi co-catalyst indeed underwent oxidation from Co(III) to Co(IV), acting as a true catalyst, even though this may not necessarily lead to an increase in the charge transfer kinetics. Through careful PEIS studies they were able to verify that water oxidation predominantly take place on the surface of Co-Pi but not on hematite. Consistent with later works by Gamelin et al. as discussed above, their results suggested the thickness of the Co-Pi catalyst was of importance to the roles the catalyst plays. From a different angle, Gamelin et al. varied the morphology of the hematite substrate and found that water oxidation could either take place on Co-Pi or directly on hematite, depending on the applied potentials.[86k] These studies together highlight the complexities of the light absorber/co-catalyst interfaces. They serve as an important basis for future studies of similar systems. Recently, we studied effects of two Ir-based water-oxidation co-catalysts on a hematite photoelectrode systematically.[86f] It was found that heterogenized molecular Ir co-catalyst could speed up the hole transfer rate but recombination rate remained unchanged (as shown in **Figure 22**). For heterogeneous $IrO_x$ co-catalyst, it not only enhanced charge transfer but also reduced surface recombination by replacing hematite/electrolyte interface. These results focusing on kinetics at the semiconductor/electrolyte interface, clear understanding of the role of co-catalyst provides a basis for further improvement.

## 8. Conclusions and Perspectives

### 8.1. Conclusions

Photocatalysis is different from conventional catalysis in the function of light, which provides energy to meet the activation needs in a large number of chemical reactions. It enables processes that are either difficult (such as pollutant oxidation) or impossible (such as thermodynamaically uphill reactions like $CO_2$ reduction) under normal conditions. The inspirations for photocatalysis can be traced back to the understanding of natural photosynthesis. Within this context, a summary of popularly studied photocatalytic systems is presented. The examples summarized here include particulate photocatalysts and complex integrated systems. The variations in their forms and complexities notwithstanding, the fundamental governing principles are shared. Further understanding and optimization of these existing photocatalysts are likely to benefit from the

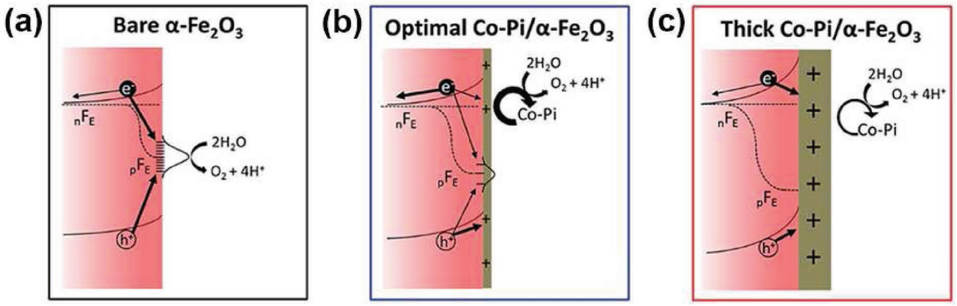


**Figure 21.** Schemes showing the charge transfer and charge recombination pathways of $\alpha$-$Fe_2O_3$ photoanodes a) and $\alpha$-$Fe_2O_3$ deposited with a thin (optimized) b), and a thick c) Co-Pi layer on their surfaces. Reproduced with permission.[163] Copyright 2016, The Royal Society of Chemistry.

summary. In describing the varying systems, we paid particular attention to how the functional components in a photocatalyst affect each other. For instance, we discussed how the introduction of co-catalyst may change the charge separation capabilities of the light absorber, and whether the co-catalyst truly acts as a catalyst in a conventional sense. Despite the over 4 decades of intense efforts, photocatalysis research still in its infancy in its development. Much is still needed for photocatalysis to make impacts to the real world. Below, we present our perspectives on how the field may benefit in the years to come.

### 8.2. Perspectives

#### *8.2.1. New Light Absorbing Materials*

The first step of photocatalysis is light absorption. For this reason, we believe the search for high-performance light absorbing materials will likely to play a critical role in future research on photocatalysis. Indeed, past efforts have identified a large number of inorganic materials, including $TiO_2$, ZnO, $SrTiO_3$, Si, $WO_3$, $Fe_2O_3$, and $Ta_3N_5$.[24c,87b] Similar to efforts in the past, while the most important considerations will still be the bandgap, which defines the ultimate efficiency of these light absorbers, factors such as stability will receive increasing attention. In addition to composition, more attention should be paid to the nanoscale features as charge behaviors in relevant length scales have been recognized as important factors, as well.[165] Though highly robust, a major challenge faced by crystalline inorganic semiconductors is that their properties are difficult to tune at wish.[166] As far as property tenability is concerned, organic semiconductors seem more intriguing but are less explored for photocatalysis. Among those that have been studied within the context of photocatalysis, g-$C_3N_4$ with a two-dimensional porous structure may be the most

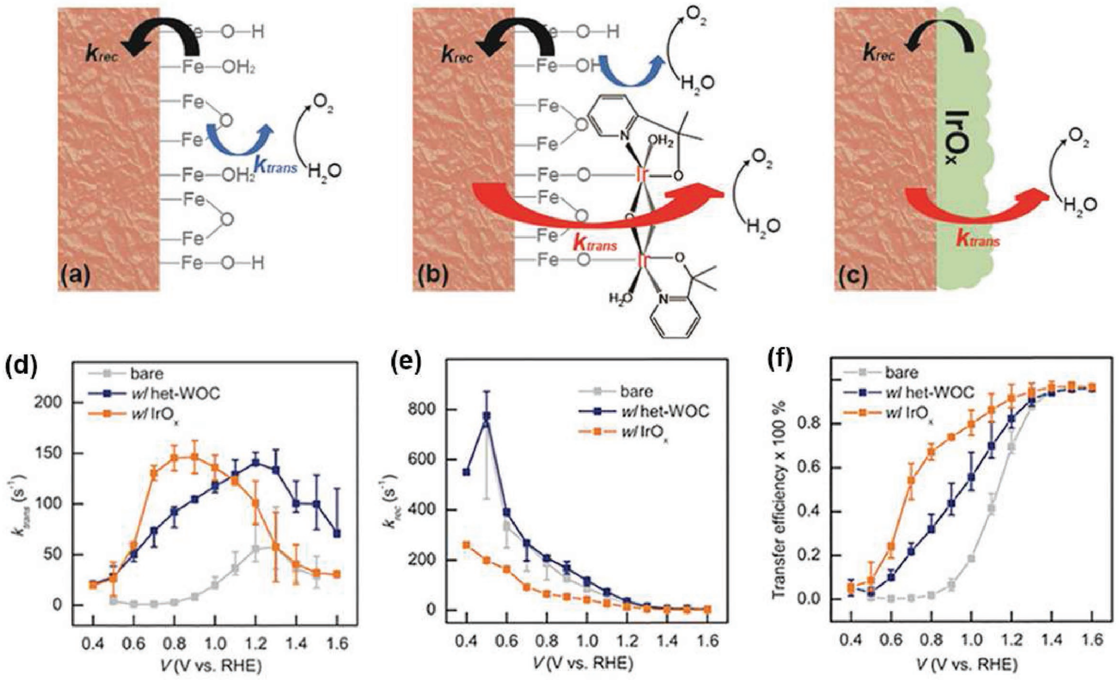


**Figure 22.** Schemes showing the kinetic models for bare hematite a), hematite with het-WOC (heterogenized molecular Ir catalyst) b), and hematite with $IrO_x$ c). d–f) IMPS data of bare hematite, hematite with het-WOC, and hematite with $IrO_x$. Charge transfer rate constants ($k_{trans}$) are shown in (d), charge recombination rate constants ($k_{rec}$) shown in (e), and charge transfer efficiencies are shown in (f).

investigated.[112c,167] Despite its promises, however, monolayer g-$C_3N_4$ remains far less active than what is theoretically predicted.[167] In addition, its low-cost, large-scale preparation has yet to be optimized. Another organic semiconductor that has piqued research interests for photocatalysis is hexagonal boron nitride (BN). Although an inherent insulator itself ($E_g$>5 eV), BN has been predicted by DFT calculations to feature desired electronic band structures for photocatalysis when doped with C.[168] Indeed, experimental results demonstrated that ternary BCN compounds exhibited catalytic activity toward $H_2$ evolution and $CO_2$ reduction under visible light irradiation better than $TiO_2$ (P25) and g-$C_3N_4$.[168b] Preliminary results like these on g-$C_3N_4$ and BCN are encouraging as they open doors to researches on light (and earth-abundant) elements. In addition, polymeric semiconductors such as linear polymers (e.g., poly-*p*-phenylene) and conjugated porous polymers show promising photocatalytic activities.[166,169] A key advantage offered by these organic semiconductors is the opportunity to guide experimental efforts in tuning their properties by theoretical and/or computational calculations. Of course, how to achieve high carrier mobility and adequate stability under photocatalytic conditions will be challenges that future research has to address.

### 8.2.2. Multi-functional Layer

As we have learned from natural photosystems, the requirements for photocatalysts are indeed incredibly complex. The chances of satisfying all these considerations on a single material are little. As such, we anticipate material design to play a critical role in future photocatalysis research. In particular, we expect the introduction of multifunctional layers, for the purpose of improving the catalytic activities and also for the purpose of stabilizing the otherwise quickly decaying photocatalysts, will become more and more common. For instance, the introduction of thin transition metal on top of Si has proven effective in enhancing the PEC stability and activity of Si.[170] In this approach, the metal layer provides protection and the surface metal oxide serves as a co-catalyst (toward water oxidation). Approaches like this, however, also introduce issues such as late $E_{on}$ due to the relatively low work function of the transition metal. Future investigations are expected to keep searching for materials that can provide the desired functionalities while addressing the related issues.

### 8.2.3. Catalysis Understanding

Photocatalysis, despite its uniqueness, is first and foremost heterogeneous catalysis. Mechanistic understanding, especially that at the molecular and atomic levels, is key to further developments. Whether and how the reactions proceed with and without light on the surface of the photocatalyst remain poorly understood. Advances in this direction will likely propel efforts to optimize photocatalysts at the molecular levels. Spectroscopic and computational studies will likely play increasingly more important roles in this direction as tools to understand the system at this scale remain limited. Insights generated by these studies will be critical to further development and may enable the development of new reaction routes. In addition, investigations into the photocatalytic pathways are important. They are expected to reveal the fundamental mechanisms and to guide further performance improvement. Efforts focused on understanding the mechanisms will be especially critical when studying photocatalysis involving multi-electron processes (such as $CO_2$ reduction), where kinetics and product selectivity are highly dependent on the reaction pathways. Furthermore, studies focused on understanding the reaction mechanisms are expected to shed light on the identification of catalytically active sites on photocatalysts. Such understanding is particularly important to organic semiconductors, whose active sites are poorly understood to date.[169] For instance, the surface terminations and defects sites on organic semiconductors are considered active toward photocatalysis, but critical details are missing. The lack of information makes it exceedingly difficult to further optimize these emerging photocatalysts. Toward this end, collaborations between experimentalists focused on understanding the mechanisms by techniques such as operando spectroscopic tools and theorists skilled with calculations are expected to yield new and exciting insights that will serve as guidelines for materials scientists to design and synthesize new, better materials.

### 8.2.4. Understanding the Interface of Different Material Components

Similar to the above mentioned understanding on the surface of the photocatalysts, mechanistic understanding at the interfaces of different components, including the light absorber, co-catalyst, passivation layers, will be critical. This is because increasingly we realize that the complex requirements for the photocatalytic functionality are most likely realized on complex, integrated systems. How these different components influence each other will become more and more important. For instance, it is not clear whether and/or how the energy is supplied (through heat or light) changes how a catalyst functions. In addition to the energetics at the interface of different material components, how the various other parameters influence the photocatalytic performance is understudied when compared with similar influences at the surfaces. For example, the details of the interfaces at the molecular level are poorly understood for most systems. The electronic states introduced by chemical impurities and lattice mismatches need to be mapped out in greater detail in order to further optimize the interfaces. How dynamic changes to the components, which is often the case for co-catalysts during chemical reactions, may change the nature of the interface is yet another important scenario to consider.

In conclusion, we see that photocatalysis is by no means a new field. It draws inspirations from natural photosynthesis and promises a direct route to photo-to-chemical energy conversion and pollutant removal. At the present stage, the challenges that limit its development are by and large issues connected to materials. These issues are complex and difficult because they simultaneously concern two distant fields of optoelectronics and catalysis. The challenges nonetheless also provide a fertile field for research, to test different hypotheses and material design principles. What has been discussed in this article only represents a general overview of the vast field, with a focus on inorganic photocatalysts. It is, nevertheless, important to note that we believe the underlying principles discussed are generic in that great inspirations can be drawn to study and improve a large class of catalytic reactions involving light as a critical energy input.

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## Conflict of Interest

The authors declare no conflict of interest.

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