Photo-Electrochemical Solar Cells

Edited by

Nurdan Demirci Sankir
Mehmet Sankir

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and Mehmet Sankir

Scrivener
Publishing

WILEY

Wiley Global Headquarters
111 River Street, Hoboken, NJ 07030, USA

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Preface

Hydrogen has a huge potential as a safe and efficient energy carrier which can be used directly in the fuel cells to obtain electricity, or be used in the chemical industry, fossil fuel processing, or ammonia production. However, hydrogen is not freely available in nature and needs to be produced. Photoelectrochemical (PEC) solar cells produce hydrogen from water using sunlight and specialized semiconductors, which use solar energy to directly dissociate water molecules into hydrogen and oxygen. Hence, it is possible to store solar energy via photoelectrochemical conversion. Besides, PEC systems reduce fossil fuels dependency and curb the exhaust of carbon dioxide. "Advances in Solar Cell Materials and Storage" series aims to provide information on new and cutting-edge materials, advanced solar cell designs and architecture, and new concepts in photovoltaic conversion and storage. *Photoelectrochemical Solar Cells*, which is the second volume of this series, compiles the objectives related to the new semiconductor materials and manufacturing techniques for solar hydrogen generation.

Discussing the underlying basics as well as the advanced details in PEC solar cell designs is highly beneficial for science and engineering students as well as experienced engineers. Additionally, the book has been written to provide a comprehensive approach in the area of the photoactive materials for solar hydrogen generation for the readers with a wide variety of backgrounds. Therefore, the book has been written by distinguished authors with knowledge and expertise about solar hydrogen generation whose contributions can benefit readers from universities and industries. The editors wish to thank the authors for their efforts in writing their chapters.

This book is organized in three parts. Part I (Chapters 1–4) covers the general concepts such as economic targets for hydrogen generation, theory and classification of PEC systems, reactor designs, and the measurements and efficiency protocols in PEC solar cells. Part I also addresses the novel hybrid structures containing inorganic/organic composites, biosensitized semiconductors, and tandem configurations. Part II (Chapters 5–8) is devoted to photoactive materials used in PEC conversion of solar energy

into chemical energy. Hematite materials, design of bismuth vanadate-based materials, copper-based chalcopyrite, and kesterite materials and eutectic composites for solar hydrogen generation are described in this part. Materials selection and photoactive electrode design are very crucial for the production of hydrogen in an efficient and economical route via PEC reaction. Therefore, the main focus of this part is to introduce the diverse range of photoactive materials especially the nanostructured semiconductors for PEC solar cells.

The book concludes with Part III (Chapters 9–11) covering photoelectrochemical-related systems. Implementation of multijunction solar cells in integrated devices for solar hydrogen generation, as well as the promising device design and the future prospects, are extensively summarized in this part. Photoelectrochemical energy and hydrogen production via dye-sensitized systems is also covered in Part III. Finally, photocatalytic formation of composite electrodes for solar cells is given in this book. Fundamentals of the photocatalytic deposition of metal sulfides on the nanostructured metal oxides, which are very promising materials for PEC systems, are summarized in the last section.

To conclude, we would like to emphasize that the second volume of the "Advances in Solar Cell Materials and Storage" series provides an overall view of the new and highly promising photoactive materials and system designs for solar hydrogen generation via photoelectrochemical conversion. Therefore, readers from diverse fields such as chemistry, physics, materials science, and engineering, mechanical and chemical engineering will definitely take advantage of this book to comprehend the impacts of the PEC solar cells.

Series Editors
Nurdan Demirci Sankır, PhD., and Nurdan Mehmet Sankır, PhD.
Department of Materials Science and Nanotechnology Engineering,
TOBB University of Economics and Technology
August 2018

Part I

GENERAL CONCEPTS AND PHOTOELECTROCHEMICAL SYSTEMS

Photoelectrochemical Reaction Engineering for Solar Fuels Production

Isaac Holmes-Gentle, Faye Alhersh, Franky Bedoya-Lora and Klaus Hellgardt*

Department of Chemical Engineering, Imperial College London

Abstract

In order for large scale photoelectrochemical (PEC) water splitting devices to be realised, a number of challenges specific to engineering must be studied, understood and overcome. A logical approach requires the deconstruction of the PEC device into a classification framework comprising two parts: the fundamental conceptual design and the engineering PEC device design. This framework was used to study common elements of photoelectrochemical reactor designs and identify the engineering challenges encountered when scaling up PEC devices. A critical review of relevant PEC reactor designs is presented, where the scalability of each is assessed and general trends are identified, indicating improvements made. Innovative reactor designs are discussed in detail and opportunities for future research directions are highlighted. Directions towards technologically and economically feasible PEC water splitting devices are outlined.

Keywords: Photoelectrochemical, engineering, scale-up, water splitting, reactor design, H_2 production

1.1 Introduction

Daily and seasonal intermittency of radiation received from the earth's ultimate energy source, the sun, is driving the search for large capacity and long-term energy storage. Solar fuels are strong candidates that share most of the qualities of conventional fossil fuels, e.g., high energy density, easy distribution and storage, and high power output. In contrast, solar fuels

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can also deliver neutral or negative carbon emissions, hydrogen being the most popular example for the former case. Splitting liquid water to produce hydrogen and oxygen using solar energy requires a minimum of 1.48 V under thermoneutral conditions. Photoelectrochemical (PEC) reactors could produce hydrogen directly using solar energy, but photoelectrode materials are yet to be identified/synthesized that are adequately efficient, durable, and scalable. To date, there is no report of a photoelectrochemical cell with only one photoelectrode capable of achieving spontaneous water splitting satisfactorily with high efficiency [1] and using a wide range of visible light. Consequently, most of the reported systems require an electrical or chemical bias to produce hydrogen at an acceptable rate. When an electrical bias is applied, the electricity can be obtained from the burning of fossil fuels or, preferably, from renewable sources such as hydro, wind, or solar energy, e.g., photovoltaic cells. In the latter case, a photovoltaic cell is integrated with a photoelectrochemical system, buried or external, to harvest the rest of the energy required [2]. Systems with more than one absorber (stacked semiconductors) could be used to supply enough energy to achieve spontaneous water splitting. These configurations are sometimes referred to as internally biased systems [1] or integrated photoelectrochemical devices [3, 4].

The engineering of photoelectrochemical devices is often overlooked, as research has been mainly focused on material development, record efficiencies, and fundamental understanding of the phenomena involved in the photon absorption and charge transfer in semiconductors and catalysts. Hence, the aim of the present work is to summarize recent developments in reactor engineering, focusing on scaled-up photoelectrochemical systems, exposing current gaps in the research literature and contrasting with technical and economic targets. The latter will be discussed briefly below with a short summary of material development, followed by a survey and description of reported designs for theoretical and fabricated photoelectrochemical reactors. In its totality, this chapter aims to define the role of the photoelectrochemical engineering in creating feasible solar fuel devices and the future challenges it will face.

1.1.1 Undeveloped Power of Renewables

The total energy demand worldwide (thermal and electrical) was 18 TW in 2014 [5]. From all renewable energy sources, only solar and wind can provide enough energy for a fully decarbonized society, with technical capacities in the order of 10^3 and 10 TW, respectively [6]. Figure 1.1 summarizes the technical power that can be harvested using current
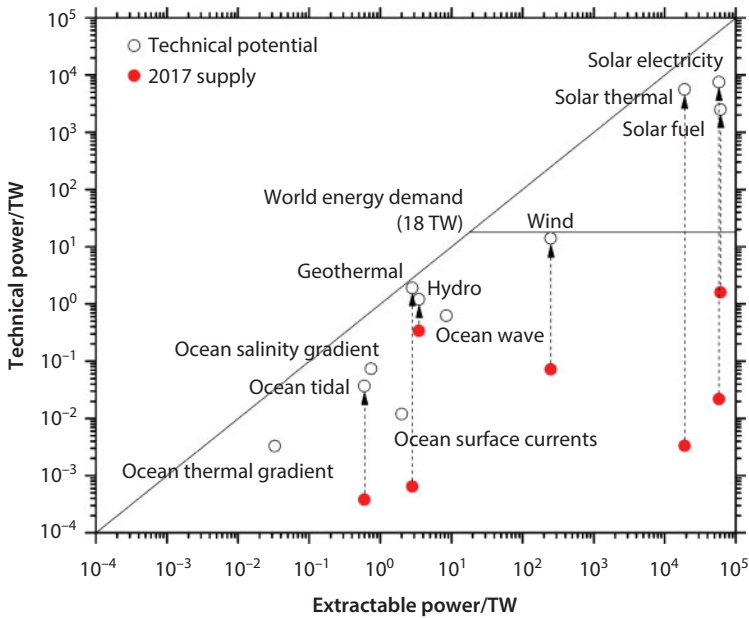
Figure 1.1 Extractable and technical potentials for several renewable sources (adapted from J. Tsao, Solar FAQs [6]).

technologies and updated supply of various renewable energy sources as previously reported by Tsao *et al.* [6] versus the extractable power from the source after chemical conversion. The present conversion and worldwide supply of solar to electricity and thermal is just above 0.02 TW, while solar to fuels dominates with a supply higher than 1 TW [7]. However, biomass is virtually the only source of solar fuels at present with arguable carbon neutrality [8]. The capacity of solar fuels, such as solar hydrogen, is still largely uncharted.

1.1.2   Comparison Solar Hydrogen from Different Sources

To date, only a few reports on the exergy efficiency and cost analysis of hydrogen production from renewable sources can be found. However, photoelectrolysis is usually not properly analyzed [9] or not analyzed at all [10, 11]. Exergy analysis is based on the second law of thermodynamics and considers the quality of the energy and not only a net energy balance. This allows a better comparison of systems that are fundamentally different, e.g., photovoltaic cells and hydroelectric power. From these reports, it was concluded that electrolysis of water using electricity from

hydroelectric power has the highest exergy efficiency (5.6%) and systems using photovoltaic cells has the lowest (1.0%) [10]. Presently, there are no reports with a proper comparison in terms of the exergy efficiency of a photoelectrochemical cell for hydrogen production.

Table 1.1 shows the expected costs of hydrogen production using conventional and already available technologies compared to those still in development [11–14]. Solar methane steam reforming is the most economical process currently deployed. These values have also been summarized by Pinaud *et al.* [14], where an estimated cost of hydrogen produced from steam methane reforming is approximately $1.25 (kg H_2)$^{-1}$, whereas the cost using photovoltaic technology is higher than $4.09 (kg H_2)$^{-1}$. In the same report, an estimated cost for hydrogen obtained from photoelectrolysis in particle-based systems was $1.60 (kg H_2)$^{-1}$, assuming 10% of solar-to-hydrogen (STH) efficiency, $4.10 (kg H_2)$^{-1}$ for concentrated panel systems with 15% STH efficiency, and as high as $10.40 (kg H_2)$^{-1}$ for an integrated PEC system with 10% STH efficiency. Recently, slightly higher costs were reported by Shaner *et al.* with PV + PEM (Proton Exchange Membrane) electrolyzer and updated costs for planar PEC devices [13]. It is obvious that the latter systems can barely compete with conventional methods and more development and research is required. The production cost of H_2 using suspended particles is expected to be the lowest among the systems under development; however, low H_2 yields, product (H_2 and O_2) crossover, and uncertain scalability are hindering further progress. Improvements in reactor design and efficiency must be made before these systems can be deployed commercially. Nevertheless, it has been stated that the production of hydrogen by photoelectrolysis is a viable option among carbon-free processes [14].

1.1.3 Economic Targets for Hydrogen Production and PEC Systems

The above prices for hydrogen contrast with the economic targets set by the US Department of Energy for solar hydrogen via photoelectrochemical water splitting as reported in Table 1.2 [16]. At present, the estimated price of hydrogen produced using integrated PEC systems is ca. $10 (kg H_2)$^{-1}$, the target by 2020 is half this value, and a fifth for the ultimate target, with a hydrogen production rate of 2×10^{-6} kg H_2 m^{-2} s^{-1}, which corresponds to a minimum current density of 193 A m^{-2} assuming a faradaic efficiency of unity. State-of-the-art photoelectrodes still perform below these values, with a record set at 85 A m^{-2} for an integrated PEC cell (GaAs/InGaP/TiO2/Ni) [17] and 140 A m^{-2} for a PV+electrolyzer system [18].

Table 1.1 Projected costs (long term) of hydrogen production.

Process	Cost/$ (kg H$_2$)$^{-1}$		
Steam reforming (Nov. 2017)	(Lemus, 2010) [15]		
Natural Gas (Market price)	1.2		
Coal (Market price)	1.8		
Designs at small-scale pilot plants	(Koumi, 2012) [11]		
Solar hybrid sulfur cycle	2.3		
Solar sulfur-iodine cycle	2.4		
Solar metal/metal oxide cycle	4.2		
Solar high temperature electrolysis	5.6		
Solar methane cracking	2.1		
Solar methane steam reforming	1.9		
Conventional renewables (Projected)	(Koumi, 2012) [11]	(Acar, 2014) [12]	(Shaner, 2016) [13]
Electrolysis using solar thermal power	3.2	–	–
Electrolysis using wind power	2.8	7.2	–
Electrolysis using photovoltaic power	7.9	9.1	12.1
Electrolysis using nuclear	-	1.3–3.5	–
Biomass gasification	1.3	1.4	–
PEC devices (Projected)	(Pinaud, 2013) [14]		(Shaner, 2016) [13]
Single bed particle suspension	1.6		–
Dual bed particle suspension	3.2		–
Fixed panel array	10.4		11.4
Tracking concentration array	4.0		9.2

Table 1.2 Targets set by US Department of Energy (DoE) [16].

Parameter	Units	2020 Target	Ultimate target
Photoelectrochemical hydrogen cost	$ (kg H$_2$)$^{-1}$	5.70	2.10
Capital cost of concentrator and PEC receiver (noninstalled, no electrode)	$ m^{-2}	124	63
Annual electrode cost per tonne H$_2$ per day	$ (t H$_2$)$^{-1}$ d^{-1} a^{-1}	255 k	14 k
Solar to hydrogen (STH) energy conversion ratio	%	20	25
1-Sun hydrogen production rate	kg H$_2$ m^{-2} s^{-1}	1.6×10^{-6}	2.0×10^{-6}

Ultimate targets also set STH efficiencies at 25% and cost of the PEC electrode at $100 per meter square, and a lifetime of 10 years. These targets prohibit the use of expensive and unstable photoabsorbers. The most inexpensive silicon-based PV modules are currently at $0.35 W^{-1} [19], with an estimated cost of $50 m^{-2} [20]. Perovskites modules are expected to be $32 m^{-2} [21], while CIGS and CdTe are between $90 and $80 m^{-2} ($0.9 W^{-1}) [20]. Multijunction, e.g., GaInP/GaAs/S, modules costs are between $4.85 and $8.24 W^{-1} depending on the type of multijunction [22] with an estimated cost between $1500 and $3000 m^{-2}.

Studies on photoelectrodes are always constrained by the compromise between efficiency and stability, the former leads to the extensive study of inefficient but scalable and stable materials, e.g., Fe$_2$O$_3$ and TiO$_2$, while record materials [18, 23, 24] are usually reported without considering in full the costs or scalability of such materials.

1.1.4   Goals of Using Hydrogen

As discussed previously, solar fuels have the advantage to be used for energy storage in a decentralized manner and when higher power output is required. Hence, its use in heavy transportation and heating is most appropriate.

The electrification of heating is constrained by the intense peaks for heat demand at well-defined times during the day, which can be 10 times higher compared to baseline in a typical UK winter day. In contrast, electrical energy peaks are generally observed at twice the baseload [25]. Hydrogen

could supply sufficient power for heating by combustion in a similar manner as natural gas or using fuel cells.

A roadmap from the International Energy Agency on the use of hydrogen in the transport sector has set economical and technical targets for the use of fuel cell electric vehicles (FCEVs) for 2050 in order to meet the decarbonization targets to limit global temperature rise to below 2 °C above the preindustrial level. This involves 25% of passenger light-duty vehicle and 10% of freight road transport running on hydrogen [26]. Studies on the energy supply to off-grid users report smaller footprint by using hydrogen-based systems (electrolyzer, fuel cell, and metal-hydride storage) compared to traditional Li-ion batteries [27]. However, this depends on the consumer needs and time and scale of storage required. In a usually forgotten market, the use of hydrogen-based energy systems for the increasing energy demands of developing countries is a plausible scenario and even regarded as the best option for these markets [28]. Besides the obvious environmental benefits of using renewable energy, solar hydrogen can also enhance the living standards of off-grid populations in developed countries.

In order to supply the hydrogen required to fulfill the demands in the aforementioned future scenarios, a durable, efficient, and inexpensive material has to be developed to be used in PEC systems. Solar-to-hydrogen efficiency is the most commonly used figure of merit, and it has been reported for a wide variety of materials. Figure 1.2 shows the updated learning curves (adapted from Ager *et al.*, 2015 [29]) classified by material for photoelectrochemical cells for spontaneous water splitting. Buried and external PV + electrolyser, with a present record of 30% [18], has dominated research in the last decades. Silicon-based systems have not seen any significant improvement in the last 10 years, mainly due to the stagnating efficiencies for this material. Efficiencies of oxide-based systems remain close to 1% values, while recent improvements on perovskites have allowed researchers at EPFL to reach efficiencies of 12.3% for a PV + electrolyser system [30]. From the materials perspective, it appears that there is less room for improvement in silicon-based PV+PEC devices, while oxides and hybrid systems are evolving fast with an extensive gap to be closed.

1.2   Theory and Classification of PEC Systems

In this section, we aim to formalize the classification of photoelectrochemical designs and terminology. The first part of this section describes the abstract conceptual design (i.e., schematic) which defines the type of system used, while the second part describes the physical structure and layout
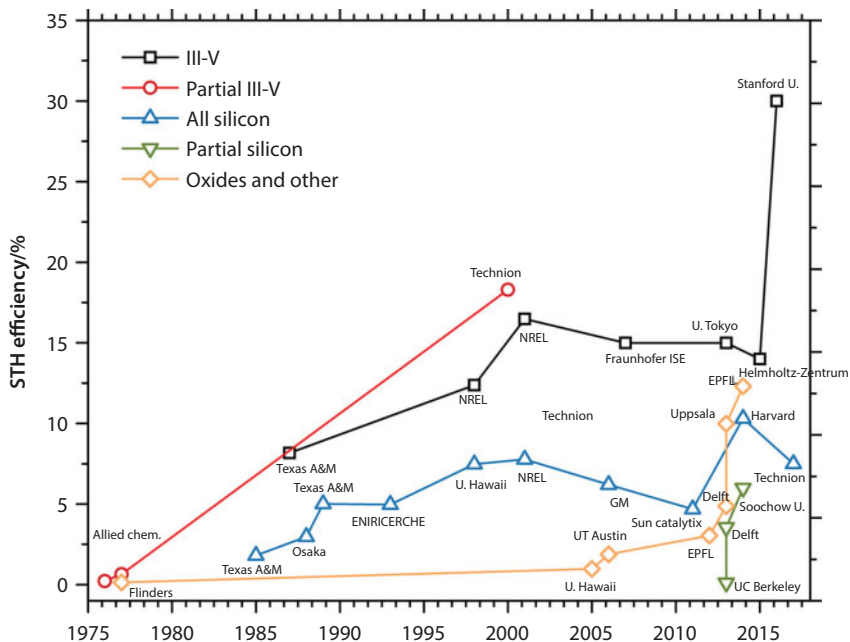
Figure 1.2 Timeline of solar to hydrogen (STH) conversion efficiencies for different materials implemented in photoelectrochemical devices for spontaneous water splitting (adapted from Ager *et al.*, 2015 [29]).

of reactor designs (i.e., engineering drawing). The rationale for this partition is to reduce the complexity in classification and to allow for reactor design grouping. Furthermore, the maximum theoretical efficiency achievable is defined by the conceptual configuration [31–33] and not the reactor design. In this work, we only discuss planar electrode systems as opposed to particulate systems due to the higher record efficiencies reported.

1.2.1   Classification Framework for PEC Cell Conceptual Design

The schematic/conceptual design of PEC systems is categorized in a hierarchical framework. The order in which a PEC system should be classified is as follows:

1. Number of photoabsorbers
2. Electrical configuration of photoabsorbers
3. Optical connection of photoabsorbers and optics of system

Any design will be characterized by these three specifications which are outlined further below.
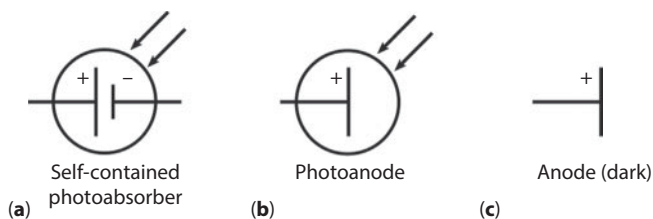
Figure 1.3 Electrical symbols where the polarity of the electrodes is in reference to an electrolytic cell.

Number of Photoabsorbers

The number of photoabsorbers used to drive photoelectrolysis has a great impact on the maximum efficiency of the system [31–33]. Unassisted water splitting with appreciable efficiencies has been achieved only by using multiple photoabsorbers [3] due to the "spectral mismatch" between the energy in the solar spectrum and the energy required to drive water splitting. Commonly, a two-photoabsorber approach is termed "a tandem cell" [34].

Photoabsorbers can be further classified by the conductive nature of the two materials that make up the electrical junction. The junction formed at two electronic conductors is commonly called a solid-state junction or photovoltaic junction, whereas the junction formed between an electronic and an ionic conductor is commonly referred to as a semiconductor–electrolyte junction. It is important to note that the electrolyte may also be a solid-state ionic conductor. An excellent taxonomy was produced by Nielander *et al.* [35], which classified the different architectures and defined a naming scheme which also differentiated between the type of the applied bias source (i.e., whether it was PV or PEC). However, for the conceptual PEC design outlined here, we only differentiate between semiconductor–liquid junction (SCLJ) in contact with the electrolyte, from which the solar fuel is synthesized and self-contained solar cell. This is to group together all systems that can bias the cell, which could include both PEC solar cells, e.g., dye-sensitized solar cells, and PV cells, e.g., multijunction III-V cells. Figure 1.3 introduces the symbols used in the subsequent sections.

Electrical Configuration of Photoabsorbers

The photoabsorbers must be placed within the electrolytic cell electrical circuit. In a generic photoelectrochemical cell, as shown in Figure 1.4, photoabsorbers can be placed at different points within the circuit. Commonly, multiple photoabsorbers are connected in series in order to generate a sufficiently large potential to split water. There is also the possibility of multiple anodes or cathodes utilizing different light absorbers as demonstrated in the work by Kim *et al.* [36].
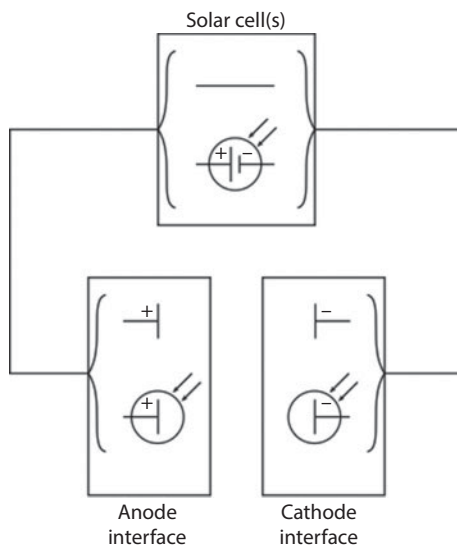
Figure 1.4 Generic schematic of layout of photoelectrochemical cell.

Optical Configuration of Photoabsorbers

For systems employing multiple photoabsorbers, there will be multiple optical configurations. Photoabsorbers can be placed in parallel or in series, which has significant ramifications for the obtainable efficiency and complexity [33]. The main advantage of optical operation in series is that a preceding absorber utilizes a portion of the spectrum and allows other wavelengths to pass through to the next absorber. Higher efficiencies can be obtained using this configuration due to a more complete capture of the spectrum of light while maintaining a more significant proportion of the captured energy of each photon. However, this approach can be complex as the spectrum must be matched to the current density and is often expensive, especially for multijunction solar cells. Optical operation in parallel is often used with photoabsorbers of the same bandgap as each solar cell can receive the portion of the spectrum needed for efficient individual operation. The photoabsorbers are then connected electrically in series in order to gener-ate the required photovoltage for water splitting if one cell is not sufficient.

In order to simplify the classification, we introduced a schematic repre-sentation of the optical pathway of light in Figure 1.5. It is important to note that at each junction where light splits (or merges), the diagram makes no assumptions about the fraction of the split and/or the spectral dependence of this. This means that complex optics such as spectral splitters (dichroic mirrors) could achieve high efficiencies through greater utilization of the
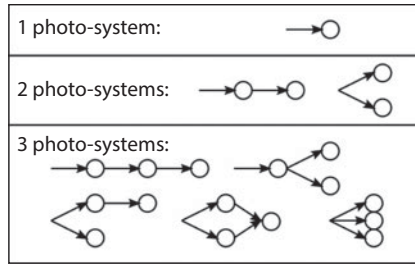
Figure 1.5 Optical configurations for 1, 2 and 3 photoabsorbers.

spectrum (similar to series configuration) while the photoabsorbers are optically in parallel.

Example Conceptual Designs

In order to demonstrate the versatility of the previously described conceptual schematic, a number of example systems from literature are presented. This methodology attempts to be a universal abstraction of the photoelectrolysis process and so can easily represent complex designs using one set of schematic rules.

The examples in Table 1.3 have been chosen to show the broad range of device architectures and the utility of the conceptual design framework outlined previously. As the number of photoabsorbers, electrical, and optical connection defines the maximum theoretical efficiency achievable, this allows for designs to be compared even though the physical implementation and materials used may differ significantly.

In this framework, photo-assisted electrolysis systems, which employ an electrical bias from an external power source (e.g., PV + transformer/inverter, wind turbine, etc.), have not been included; however, they could be easily implemented. As the mode of the external power source is irrelevant from a PEC conceptual design viewpoint, it could simply be included as a power source symbol.

1.2.2   Classification Framework for Design of PEC Devices

For a conceptual PEC cell design to be engineered into a physical device, a number of considerations must be made as to the placement of components within the cell. The framework outlined below classifies each device design.

1. Conceptual design (see previous section)
2. Electrode construction

Table 1.3 Example conceptual designs.

Paper	No. of photoabsorbers	Electrical configuration	Optical configuration	Information about photoabsorbers
Han et al. 2014 [37]	3			1) W:BiVO$_4$ 2) a–Si:H 3) nc–Si:H
Khaselev and Turner 1998 [38]	2			1) GaAs 2) GaInP$_2$
Jia et al. 2016 [18]	3			1) InGaP 2) GaAs 3) GaInNAs
Jacobsson et al. 2013 [39]	3			1) CIGS 2) CIGS 3) CIGS
Kim et al. 2016 [36]	2			1) BiVO$_4$ 2) Fe$_2$O$_3$