# Harvesting light with semiconductor: Role of interface in the processes of charge transfer

Olivier Nguyen, Natacha Krins, Christel Laberty-Robert*

*Sorbonne Universités, UPMC Univ Paris 06, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 4 Place Jussieu, 75005 Paris, France*

## A R T I C L E   I N F O

## A B S T R A C T

Photoelectrochemical devices are a promising approach to produce scalable and sustainable carbon-free energy. One of the challenges is to find the adequate Earth abundant semiconducting photoelectrodes able to harvest light, store it and convert it into electricity. To design efficient electrodes, there is a need to understand the physicochemical properties of the semiconductor, the chemical and the structure of the interfaces and the transfer mechanisms at these interfaces. The aim of this review is to summarize recent progress and open challenges in i) the bulk physicochemical properties of the semiconductor, ii) the chemical and energetic dynamics of the electrode/electrolyte interfaces and iii) the development and relevant use of operando techniques to understand transfer mechanism at these interfaces.

## 1. Introduction

Converting sunlight into either electricity or fuel through photoelectrochemical devices offers a promising approach for producing scalable and sustainable carbon–free energy [1,2]. A key aspect to building an efficient photoelectrochemical cell (PEC) is to find earth-–abundant semiconducting photoelectrode materials able to absorb sunlight and drive, for example, water splitting reactions to produce hydrogen. Recent developments show that photoelectrodes can absorb sunlight to store energy through insertion reactions (photorechargeable battery, i.e. where charge is driven by light).

A large number of semiconductors have been explored as photoelectrode absorbers, including metal oxides, group III–V semiconductors and chalcogenides for water splitting application [3]. Nevertheless, despite steady efforts and some breakthroughs, no single material has yet been found that simultaneously satisfies the efficiency and the stability required for the widespread commercialization of hydrogen technology [4]. For instance, the lifetime of highly efficient perovskite-based PECs is rather limited due to the instability of the materials in aqueous solutions [5]. As a consequence, extensive effort has been directed towards the development of complex PEC architectures that integrate multi–junction absorbers with catalysts and protective insulating layers. These efforts aimed at improving the stability and solar–to–hydrogen conversion efficiency [6–9]. In addition, tuning materials parameters such as crystal phases, composition, morphology, surface chemistry, and defects has been shown to significantly improve the performance of PECs.

With the growing complexity of PEC architectures, understanding the properties of the interfaces between its components (i.e. solid/solid and solid/liquid) is key to predict novel, better performing materials, and eventually for efficient solar–to–hydrogen production (STH). In this regard, rapid charge transfer between the photoelectrode (and potentially catalysts and/or protective layers) and the electrolyte will be dictated by the electronic and structural properties of absorbers/electrolyte interfaces. In addition, structural properties and chemical reactivity, including electrochemical corrosion, photocorrosion, and dissolution of photoelectrodes and catalysts in aqueous solutions, need to be controlled to improve the durability of PEC cells.

Interfacial structural and electronic properties of PECs are of course intertwined. For example, band edge positions of photoelectrode absorbers depend on the surface termination, the reconstruction and the concentration of impurities and defects [10]. In addition, the stability of the photoelectrodes against oxidation (reduction) is determined by the relative energy between their valence band maximum (conduction band minimum) and intrinsic oxidation (reduction) potential [11]. It is difficult to explain these phenomena, especially due to challenges related to structural characterization of the dynamic interfaces.

The goal of this paper is to summarize recent progress and open challenges in describing how light affect the electrical properties of semiconductor and modify the electrode/electrolyte interfaces. It will focus on the interplay between structure, chemical composition and photoelectrochemistry. We first briefly describe the impact of light on semiconductor. We then discuss the dynamics of the structural and electronic properties of photoelectrode/electrolyte interfaces. Finally,

---

* Corresponding author.
  *E-mail address:* christel.laberty@upmc.fr (C. Laberty-Robert).

challenges in understanding the mechanisms at the interfaces using classical and operando techniques are summarized, together with our conclusions.

## 2. Tuning the properties of semiconductors

The selection of the semiconductor electrode is important when designing efficient photoelectrochemical device. The electrode materials have to satisfy a number of requirements depending on the application. However, whatever the electrochemical device considered, the photoelectrodes should exhibit proper band gap to have a strong visible light absorption. During this step, $e^-/h^+$ photocarriers are generated. To efficiently harvest light, the $e^-/h^+$ recombination should be avoided and this can be tuned through a careful control of the semiconductor structure, its chemical composition (bulk and surface) as well as its microstructure. For example, in water splitting, the photoelectrodes should exhibit (i) a proper band gap energy ($\sim$ 2 eV) to cover water dissociation energy (1.23 eV) and a strong visible light absorption, (ii) band edge positions enabling oxidation and reduction of water (0 and 1.23 V vs. RHE, respectively), (iii) chemical and electrochemical stability under illumination in water, (iv) fast transport of the photogenerated electrons and holes in the semiconductor, (v) low over-potentials for the electrode reactions and (vi) low cost. In many semiconductors, one major drawback that limits the performances is the $e^-/h^+$ recombination due to the poor charge carrier transport (short diffusion length). To overcome this limitation, several strategies have been explored including metal or metalloid doping and nanostructuration. Modification of interfaces has been also tested but will not be discussed in this review.

### 2.1. Impact of doping on the photoelectrochemical properties

To improve the photoelectrochemical performances, a lot of work has been dedicated to the modification of the chemical composition of the semiconductor [12–16]. Doping on either the transition metal or the metalloid has been investigated to tune both the band-gap [17] and the electrical properties of the semiconductor. Nitrogen–doping has been extensively investigated to adjust both the optical and electrical properties of the well-known $TiO_2$ anatase [15,16]. Studies demonstrated that both the doping element and the doping concentration appear to be critical. In nitrogen–doped $TiO_2$, the N-substitutional states close to the valence band gap of $TiO_2$ narrow the optical absorption edge, causing the well-established activation of $TiO_2$ in the visible range. However, increasing the nitrogen concentration in the $TiO_2$ lattice has also a negative effect, as a decrease of the overall quantum efficiency is observed due to an increase of the electron–hole recombination sites [15].

Doping on transition metal has been proven to be efficient for improving the performances of classical photoanodes including $Fe_2O_3$ [18–22], $WO_3$ [23–28] and $BiVO_4$ [12,29–34]. It is mainly due to the enhancement of their electrical properties. Hematite ($\alpha$-$Fe_2O_3$) is one of the most popular photoanode materials because of (i) its small band gap ($\sim$ 2.1 eV) that allows an important theoretical solar–to–hydrogen efficiency of 15.3% (or photocurrent generation of 12.6 mA/cm$^2$ at 1.23 V vs. RHE under 1 sun illumination), (ii) its excellent stability in alkaline conditions, (iii) its low price, and (iv) its environmentally benign characteristics [35–37]. However, performances of photoelectrodes made of pure hematite are poor, because of its low absorption coefficient due to its indirect band gap and its extremely poor electrical conducting property with a hole diffusion length of only 2–4 nm [38]. Excessive charge recombination in the electrode was then measured. To reach slower recombination process, n– or p–type doping are commonly investigated. Both an augmentation of photocurrent and STH efficiency have been demonstrated, and attributed to the modification of their electrical properties [39]. An example of improvement of photochemical properties is given for Sn–doped hematite in Fig. 1.1.

This strategy has also been extended to bismuth vanadate ($BiVO_4$)

photoanode [32]. Even if $BiVO_4$ photoanode is a very promising material because of its bandgap of 2.4 eV, the first efforts in this direction have been hampered by its low efficiency, with photocurrent lower than 1 mA/cm$^2$ in Air Mass 1.5 (AM 1.5). Its performances have been greatly enhanced by modifying its electron conductivity. The positive effect of doping is summarized in Fig. 1.2. This figure shows that the 1% W–doped $BiVO_4$ (red curve) significantly exhibits higher photocurrents than the undoped film (black curve). The amount of doping should be carefully controlled. In this study, an optimum of 1% W is necessary to achieve the best performances. A lower concentration does not provide enough free electrons, whereas a higher concentration reduces the photocurrent owing to lattice strain, to $WO_3$ phase segregation, or even to a modification of the space charge region width. The latter is the region where the separation of photo–generated electrons and holes occurs due to the presence of an electrical field (applied potential).

### 2.2. Impact of architecture/morphology on the photoelectrochemical properties

Increasing the interfacial area between the electrolyte and the semiconductor through nanostructuration, would facilitate the charge collection. Indeed, it tends to enhance the probability of an absorbed photon to be within the hole transport length of the semiconductor–liquid junction, thereby preventing $e^-/h^+$ recombination.

In water splitting, a lot of studies have been dedicated to modifying the nanostructure of hematite photoanode for improving photon harvesting efficiency. Different morphologies including nanorods [40,41], nanowires [42,43], arrays [44], nanoflakes [45] and porous colloidal based films [36,46] have been investigated. 1D nanostructure tends to enhance electron mobility and quantum efficiency [47]. In the case of $TiO_2$ nanotubes (TNT), an increase in electron mobility compared to conventional $TiO_2$ nanoparticles and quantum confinement's effects have been observed. 1D design will overall limit the recombination of photo–induced $e^-/h^+$ pairs [48]. In the nanotube architecture, both its length (L) and wall thickness (d) appear to greatly impact the performances (Fig. 2.1, 2.2, 2.3). When light is absorbed, the photogenerated electrons diffuse from their generation site, along the nanotube, to the TNT/substrate interface. They are then collected to the counter electrode and *in fine* contribute to the photocurrent. Lynch et al. [49] demonstrates that the nanotube length (L) has to be adjusted according to the penetration length of incident light at a certain wavelength ($L_\lambda$) and to the majority carrier length ($L_n$). Photogenerated holes have to reach the TNT/electrolyte interface, travelling perpendicularly to the nanotube length. The wall thickness (d) should then be smaller than the diffusion lengths of holes, corrected by the width of the depletion layer. The enhancement in the performances can be more important when combining nanostructure and chemical modification. This is illustrated in Figs. 2.4, 2.5, 2.6.

In thin film electrode, the microstructure of the electrode, *ie.* porous vs. dense, does also impact photocurrents. Recently, Hilliard et al. [50] demonstrated that $WO_3$ mesoporous films exhibit larger photocurrents than the dense ones, due to the important specific surface area of mesoporous films that limit $e^-/h^+$ recombination. At AM1.5 G conditions, a photocurrent of 0.4 mA cm$^2$ has been measured for roughly 550 nm mesoporous $WO_3$ thin films. It is important to keep in mind that nanostructuring can also increase surface recombination and lower the surface photovoltage, thereby limiting the performances [51]. Chemseddine et al. [52] demonstrated in their solution–processed multi-layered $BiVO_4$ photoanode that the crystallinity of the films governs its performances more than the morphology of the film. Highly crystalline films with adequate thickness and particles size and connectivity showed improved carrier separation efficiencies.

Other strategies including nanophotonic structures have also been investigated to improve light harvesting efficiency as it allows confining light at the nanometer scale. An optical cavity can reduce the thickness of photoelectrodes without compromising their light absorption.