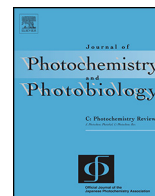




Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology C: Photochemistry Reviews

journal homepage: [www.elsevier.com/locate/jphotochemrev](http://www.elsevier.com/locate/jphotochemrev)

Invited Review

## Molecular cathode and photocathode materials for hydrogen evolution in photoelectrochemical devices



Nicolas Queyriaux<sup>1</sup>, Nicolas Kaeffer<sup>1</sup>, Adina Moroza<sup>1</sup>, Murielle Chavarot-Kerlidou, Vincent Artero\*

Laboratoire de Chimie et Biologie des Métaux, Université Grenoble Alpes, CNRS, CEA, Life Science Division, 17 rue des Martyrs, 38000 Grenoble, France

### ARTICLE INFO

#### Article history:

Received 26 June 2015

Received in revised form 28 July 2015

Accepted 3 August 2015

Available online 7 August 2015

#### Keywords:

Hydrogen

Catalysis

Bio-inspiration

Artificial photosynthesis

PEC devices

### ABSTRACT

Storage of solar energy in the form of readily available easy-to-handle fuels is the main bottleneck toward the development of a carbon-neutral alternative energy. Taking inspiration from natural systems, artificial photosynthesis is a technology to be for efficiently converting the tremendous solar energy received every day on Earth into chemical energy, *i.e.* fuels. In particular, hydrogen production through light-driven water splitting is the subject of numerous investigations. We focus here on the construction of electrodes and photoelectrodes achieving H<sub>2</sub> evolution, as components of photoelectrochemical (PEC) cells. In such devices, H<sub>2</sub> evolution at the cathode or photocathode is combined with water oxidation to oxygen at the photoanode or anode. We review here the various molecular-based materials developed in this context with emphasis on those specifically exploiting the properties of Earth-abundant elements.

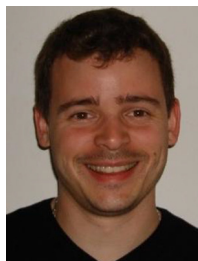
© 2015 Elsevier Ireland Ltd. All rights reserved.

### Contents

1. Introduction.....	91
2. Overview on photoelectrochemical devices for water splitting.....	91
3. Molecular H <sub>2</sub> -evolving cathodes.....	93
3.1. Entrapment of the catalyst within a polymeric material.....	94
3.2. Covalent attachment of the catalyst within an oligomeric or polymeric material.....	94
3.3. Non-covalent attachment of the catalyst <i>via</i> $\pi$ stacking interactions.....	97
4. Molecular H <sub>2</sub> -evolving photocathodes based on solid-state semiconductors.....	97
5. H <sub>2</sub> -evolving photocathodes based on organic semiconductors.....	100
6. Dye-sensitized molecular H <sub>2</sub> -evolving photocathodes.....	101
7. Conclusion.....	103
Acknowledgements.....	103
References.....	103

\* Corresponding author.

E-mail address: [vincent.artero@cea.fr](mailto:vincent.artero@cea.fr) (V. Artero).<sup>1</sup> These authors equally contributed to the paper.



**Nicolas Queyriaux** is a graduate of the Ecole Normale Supérieure (Ulm) and of the University Pierre et Marie Curie (Paris 6). He joined in 2012 the Life Science Division of CEA as a graduate student in the group of Dr Vincent Artero with a project related to the design of new photo- and electro-catalysts for hydrogen production and their subsequent grafting onto conducting surfaces.



**Nicolas Kaeffer** received both a Chimie ParisTech engineer diploma and a master level in molecular chemistry from the Université Pierre et Marie Curie (Paris 6) in 2012. Since then, he works as a graduate student in CEA-Grenoble, on the construction of molecular cathodes and photocathodes for hydrogen evolution based on cobalt diimine–dioxime complexes, under the supervision of Dr Vincent Artero.



**Adina Moroza** received her PhD from the University of Bucharest in 2007. From 2009 to 2013 her research activity at CEA Saclay and ICGM in Montpellier has been focused on non-precious metal catalysts for the oxygen reduction reaction in fuel cell. She joined in 2014 the group of Dr. Vincent Artero to work on the development of photocathodes for hydrogen production and to study electrocatalytic processes.



**Murielle Chavarot-Kerlidou** studied organic chemistry at the University of Grenoble (PhD 1998) and obtained a CNRS position (2002) to develop organometallic chemistry in Paris, from where she moved in 2009 to join CEA-Grenoble and work on hydrogen photoproduction.



**Vincent Artero** studied at the Ecole Normale Supérieure (Ulm) and graduated in inorganic chemistry at the University Pierre et Marie Curie in Paris (PhD 2000). After a post-doctoral stay in RWTH Aachen in the group of Prof. U. Kölle, he moved to the CEA center in Grenoble (Life Science Division) in 2001 to develop bioinspired chemistry related to hydrogen production and artificial photosynthesis. He received the “Grand Prix Mergier-Bourdeix de l’Académie des Sciences” (2011) and was granted in 2012 with a Starting Grant from the European Research Council (ERC).

## 1. Introduction

There is now a consensus on the urgency to diversify the energetic mix of our societies by the introduction of a growing amount of renewables. Because of the availability of sunlight at the surface of Earth, solar energy research is the spearhead of these new non-carbon based energy technologies. It has recently been shown that, among all other renewable energy sources, only solar energy would be able to provide the additional >14 terawatts required by our societal needs by 2050 [1,2]. However, this additional energy input must be stored in a durable way because of the mismatch between solar energy intermittence and economic/domestic demand. In that prospect, producing fuels from readily available resources such as water is probably the only sustainable way to go. Hydrogen

production through water splitting thus appears as an attractive solution to store the abundant flow of sunlight falling on Earth. This clean energy carrier can then be used to produce electricity on-demand in fuel cells with very high energy conversion efficiencies [3]. A close-to-market way to convert solar energy into hydrogen is to interface photovoltaic technologies with water electrolysis. However, such a solution remains expensive and still needs further technological developments. Alternatively, direct utilization of sunlight, *i.e.* without intermediate production of electricity, to split water into oxygen and hydrogen in a single device would be a major breakthrough in hydrogen production, as far as mass production costs are concerned [4–6]. A recent life-cycle net energy assessment has shown that such devices can be economically viable when developed at large scale if they exhibit a solar-to-hydrogen yield superior to 5% and a stability over 10 years [7]. Anticipated costs for H<sub>2</sub> production are in the range of \$2–4 per kg H<sub>2</sub> [8].

A major issue related to both reductive and oxidative processes involved in water splitting, *i.e.* the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), resides in their multielectronic nature, resulting in strong kinetic limitations. This bottleneck requires the development of efficient electrocatalysts, proceeding at high rates and low driving force, called overpotential. So far, the most efficient electrocatalysts are based on noble metals, in particular platinum for both HER and OER and iridium or ruthenium oxide for OER. However, the utilization of Pt and Ir-/Ru-based catalysts in technological devices for worldwide energy supply is not sustainable because of their scarcity in Earth crust’s and their related high costs [1,9,10]. Intense research activity in this field during the last two decades has led to the development of new electrocatalytic materials based on non-noble metals [11–13] including both solid state materials and molecular catalysts. In this review we almost exclusively focus on the later series and limit our scope to hydrogen evolution. Similar approaches that include biomolecules such as enzymes and photosystems will not be discussed here [14–17]. After a general introduction on photoelectrochemical devices, we describe how catalysts can be immobilized onto cheap carbon-based materials so as to prepare active cathodes for HER. We then consider their integration into photocathode materials, where the photoactive component can be solid-state inorganic semiconductors, organic semiconductors or molecular photosensitizers. As a final step, we point out few recent attempts toward the build-up of overall water-splitting cells which include such molecular-based photocathodes.

## 2. Overview on photoelectrochemical devices for water splitting

Building photoelectrochemical cells (PECs) is not a straightforward procedure. Several architectures have been identified, each of them presenting its own advantages and drawbacks. We present below an overview of these possible architectures.

The simplest configuration involves a single photoactive component, usually coupled to the OER catalyst as described in Fig. 1a. The resulting photoanode, reproducing the function of Photosystem II during biological light-driven water-splitting processes in photosynthetic microorganisms, uses solar energy to extract electrons from water which is oxidized to O<sub>2</sub>. Then, the electrons generated at the photoanode are collected at the cathode where a catalyst evolves H<sub>2</sub>. Proton transfer through the electrolyte and possibly through a membrane ensuring the separation of H<sub>2</sub> and O<sub>2</sub> gases allows for the mass balance in the whole device. There is no fundamental reason why a similar architecture with the light-harvesting unit connected to the HER catalyst could not be considered [18]. The resulting system (Fig. 1b) then combines an anode with a photocathode. Nevertheless, in most cases, the use

Download English Version:

<https://daneshyari.com/en/article/31262>

Download Persian Version:

<https://daneshyari.com/article/31262>

[Daneshyari.com](https://daneshyari.com)