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Production of electricity and hydrogen by photocatalytic degradation of organic wastes in a photoelectrochemical cell
The concept of the Photofuelcell: A review of a re-emerging research field

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ABSTRACT

The present review aims to give to a researcher who has no experience with Photofuelcells all necessary basic knowledge to join the field without much trouble and to give to an experienced researcher a handy manual of reference. The author has dealt with the principal matters related with the design of a photoelectrochemical cell and the factors that affect efficient production of electricity by photocatalytic degradation of (principally) organic and (secondarily) inorganic waste materials. A large portion of the paper is devoted to the review of materials used for making a photoanode since most of the accomplished research is on this exact matter. The paper also briefly reviews the materials used to make the rest of the components of the cell as well as the models of cell efficiency and photodegradation procedures during cell operation.

Contents

Abbreviations: CB, Conduction band; E_g, Energy gap, Band gap; EQE, External quantum efficiency; FF, Fill factor; FTO, Fluorine-doped tin oxide; I_{sc}, Short-circuit current; IPCE, Incident photon to current conversion efficiency; IQE, Internal quantum efficiency; ITO, Indium-tin-oxide; J_{sc}, Short-circuit current density; NHE, Normal hydrogen electrode; PC, Photocatalytic; PEC, Photoelectrochemical; PFC, Photofuelcell.; PV, Photovoltaic; QD, Quantum dot; R_{ct}, Charge transfer resistance; VB, Valence band; V_{oc}, Open-circuit voltage.

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1. Introduction

Production of electricity and hydrogen by photocatalytic degradation of organic wastes in a photoelectrochemical (PEC) cell is an attractive project with double environmental benefit: waste material can be consumed and solar radiation can be converted into useful forms of energy, such as electricity and hydrogen. This idea is not new but a large re-emerging interest is recently expressed. Photocatalytic hydrogen production by photodegradation of organic wastes is shadowed by the more popular idea of water splitting. In fact, these two matters are studied in parallel while the basic photocatalytic setups are similar, so that in essence, they constitute one single field of research and they have the same origins. The most celebrated scientific publication that affected the development of the field was the work by Fujishima and Honda [1] in 1972, describing photocatalytic water splitting in a PEC cell using a semiconductor (rutile single crystal) electrode. This work has been the point of reference for many later research efforts [2–10], including the recent ones [11–17]. Since then, a huge amount of research has been published. After the original excitement, interest has later somehow faded [18]. However, the broad experience accumulated for more than 30 years of studies on photocatalytic degradation of organic substances [19–46], the development of new nanostructured photocatalysts, the optimization of methods of material deposition and, generally, the impressive progress of Materials Science in combination with the increasing awareness on the environmental issues have created new excitement about this field. The present review does not intend to cover all related published works but to focus on some characteristic publications and to mark the major tendencies so as to offer to readers an easy to grasp but integral view of the field.

2. Definitions

Production of hydrogen by degradation of organic substances in the presence of a photocatalyst can be distinguished into two major categories:

(1) *Photocatalytic (PC) production of hydrogen*:By this term, we usually mean production of hydrogen by heterogeneous photocatalysis using powdered or supported, pure or combined photocatalysts. As shown in Fig. 1A, the photocatalyst is excited by absorption of photons, which create electron–hole pairs. Holes oxidize the photodegradable substance, either directly or through radical intermediates, typically $OH^{\bullet}$, which are very efficient hole scavengers. Oxidation liberates hydrogen ions, which can be reduced by photogenerated electrons producing molecular hydrogen [9,19,43,47–59]. The photodegradable substance can simply be water itself; however, the product of oxidation of water is oxygen, which interacts with hydrogen regenerating water. Thus it is difficult to produce hydrogen by photocatalytic water splitting, since hydrogen and oxygen must be spatially separated. This can be only managed in a PEC cell, as it will be explained below. As a matter of fact, in order to detect photocatalytically produced hydrogen, it is necessary to apply conditions of absence of oxygen. Thus photocatalytic production of hydrogen is usually monitored by inert gas flow [56,58,59]. Photocatalytic production of hydrogen, in the above sense, will not be the main focus of the present paper.

(2) *Photoelectrochemical production of hydrogen*: In this case, hydrogen is produced in a PEC cell. The following three components are the main components of a PEC cell: (a) The anode electrode, which carries the photocatalyst and thus it is usually named "Photoanode". When the photocatalyst is an n-type semiconductor, which is almost the exclusive case, the photoanode produces electrons, i.e. it is the negative electrode. Oxidation reactions take place at the photoanode; (b) The cathode electrode, which carries the electrocatalyst, i.e. a material, which facilitates transfer of electrons from the cathode to the liquid phase. Reductive interactions take place at the (dark) cathode, for example, reduction of hydrogen ions to molecular hydrogen; (c) The electrolyte, which is added in order to increase conductivity and define the pH. The photoelectrochemical production of hydrogen is schematically illustrated in Fig. 1B. Photons are absorbed by the photoanode generating electron–hole pairs. Holes oxidize the photodegradable substance, as above, liberating hydrogen ions, which diffuse in the liquid phase. Electrons are channelled through an external circuit towards the cathode, where they reduce hydrogen ions producing hydrogen molecules [11]. Thus production of hydrogen is accompanied by flow of electrons, i.e. an electric current, in the external circuit. Hydrogen, of course, is detected in the absence of oxygen. Otherwise, in its presence, hydrogen is retained regenerating water. Water splitting in a PEC cell leads to hydrogen production, since the oxidation site, i.e. the photoanode, is spatially separated from the reduction site (cathode), thus O_2 and H_2 can be easily separated [11,12,15].

2.1. The Photofuelcell

In the presence of oxygen, for example, aerated liquid phase, no hydrogen can be detected. In that case, current can still flow in the external circuit of the PEC cell. Electrons arriving at the cathode reduce O_2 (cf. Section 3). Then the cell acts as a Photofuelcell (PFC). This term, in this or in slightly modified form, is recently gaining more and more ground [13,14,17,60–64]. A PFC consumes an

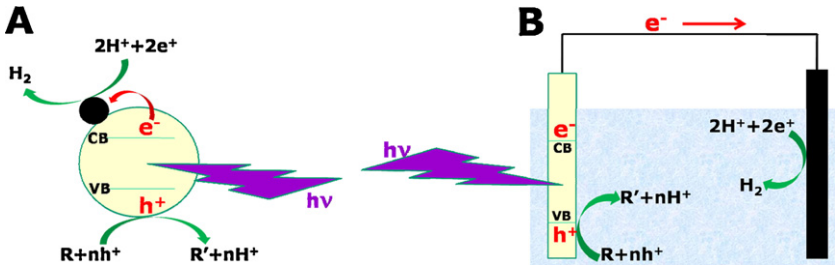

Fig. 1. Schematic representation of the photocatalytic (A) and the photoelectrochemical (B) production of hydrogen. The black full circle in (A) represents a co-catalyst (usually, a noble metal nanoparticle). The co-catalyst scavenges photogenerated electrons. In (B), anode electrode is on the left side and cathode on the right side. Oxidation and reduction may only take place when the photogenerated electron-hole pairs possess the necessary oxidation/reduction potential.