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An innovative photoelectrochemical lab device for solar water splitting

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ABSTRACT

A photoelectrochemical (PEC) device capable of splitting water into storable hydrogen fuel by the direct use of solar energy is becoming a very attractive technology since it is clean and sustainable. Indeed, real field experiments are being developed in order to assess technological issues for large-scale usage under outdoor conditions. Following the need for developing photoelectrochemical devices with an optimized design that allows reaching a commercial performance level, the present works describes an innovative PEC cell for testing different photoelectrodes configurations, suitable for continuous operation and for easily collect the evolved gases. Moreover, a porous Teflon® diaphragm useable for a wide range of aqueous electrolyte solutions is tested. Two semiconductors were investigated: tungsten trioxide and undoped hematite. The WO_3 photoelectrodes were deposited in two different substrates: (i) anodized WO_3 photoelectrodes on a metal substrate and (ii) WO_3 deposited by blade spreading method on a TCO glass substrate. The undoped-Fe_2O_3 photoanode was deposited by ultrasonic spray pyrolysis technique in a TCO glass substrate. The material deposited on glass substrates allows to obtain transparent photoelectrodes. Photocurrent–voltage characteristics were obtained for all samples characterized under three different conditions: (i) no membrane separating the anode and the cathode evolution; (ii) using a Teflon® diaphragm and (iii) using a Nafion® 212 membrane. The transparent samples (photoanodes deposited on glass substrates) produced the highest values of photocurrent when the Teflon® diaphragm was used. This photocurrent enhancement was assigned to the high reflectance showed by the diaphragm, which reflects back a significant fraction of the transmitted solar radiation.

1. Introduction

Finding alternatives to supply the world energy needs by developing clean and safe processes for energy production without CO_2 emissions is currently a key issue. According to different sources, the energy demand will almost double until 2050, from 13 TW to 23 TW. With approximately 120 PW of solar energy continuously irradiating the surface earth, the sun seems to be an outstanding source of energy to overcome the current and future energy demand [1]. Currently, only 1% of the total consumed energy comes from the sun, mainly through the use of photovoltaic (PV) technology [2]. The electrical photovoltaic power, however, is not dispatchable and, thus, a complementary approach is needed to transform the solar radiation into a storable energy form for later use [3]. One of the most interesting technologies is the photoelectrochemical (PEC) cells that combine in a single device the harvesting of solar energy with an electrolysis system, converting water into hydrogen and oxygen by light-induced electrochemical processes [4]. Presently, the main concerns about PEC cells lie not only on the energetic properties and stability issues, but also on the efficiency improvement of the photoactive materials in order to attain at least 10% of energy conversion efficiency; this is the minimum efficiency level required to make the PEC solution commercially interesting/viable [5].

There are numerous hydrogen-production approaches that use solar energy for PEC water splitting: (i) combined PV-electrolysis system; (ii) photoelectrode-based systems; (iii) photocatalysts based slurry systems. The first work reporting successful water splitting by bandgap excitation of TiO_2 in a PEC cell configuration using a Pt wire as counter-electrode dates back to the earlier 1970s, by Fujishima and Honda [6]. Afterwards, a monolithic photoelectrochemical/photovoltaic cell (PEC/PV cell) placed in series using heterojunctions of expensive and instable III–V materials, such as $GaInP_2$ and *n-p*-GaAs, demonstrated 12.4% efficiency of light conversion into hydrogen [7]. More recently, a single photoelectrochemical device with Pt-doped hematite photoanode modified with Co–Pi catalyst produced a record-performance of 4.32 mA cm^{-2} at 1.23V_{RHE} under simulated 1 sun (100 mW cm^{-2}) [8]. A different approach for splitting water into hydrogen and oxygen consists of using aqueous suspensions of

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self-supported photocatalysts composed by semiconductor powders or colloidal (often a large band gap metal oxide) and a noble metal such Pt [9]. Even if these systems present the great advantage of enabling photolysis in a homogeneous phase without the need of both expensive transparent electrodes and directional illumination, they have a huge problem: the separation of the explosive mixture of hydrogen and oxygen is not easy, bringing safety concerns about these devices [9].

All the above mentioned options have the particularity of combining the harvesting of solar energy and the electrolysis of water into a single conversion unit called PEC cell. Although the PEC cell approach is simple and elegant in concept, in practice it is very challenging since it relies on complex interactions involving sunlight, semiconductors and liquid solutions [10,11]. In fact, PEC cell researchers claim that these systems are the *Holy Grail* of hydrogen production since it offers a unique combination of an efficient and low-cost approach for producing high purity hydrogen from water by harvesting solar energy [10]. Nowadays, powerful synergies are being created between researchers from different fields to pursue the PEC quest [12].

Among the different examples presented above, the most studied topic is the photoelectrode-based systems, where the water splitting phenomenon produces oxygen and hydrogen at a physically separated anode and cathode, respectively [9]. Here, either or both electrodes can be photoactive and the evolved gases can be collected and stored separately. Currently, the major challenge in developing efficient PEC cells for water splitting relies on finding inexpensive materials that fulfill as much as possible the requirements of an ideal photoelectrode: (i) it has to have strong light absorption in the visible spectrum, (ii) high chemical stability in aqueous electrolyte solutions under dark and illuminated conditions, (iii) suitable band edges positions for hydrogen and oxygen evolutions, (iv) low kinetic overpotentials; and finally (v) the charge transfer at the semiconductor/electrolyte interface must be selective for water splitting (Fig. 1) [13,14].

Oxide semiconductors (both n- and p-type) have been shown to be promisingly stable photoelectrodes for electrolysis of water. The most frequently studied photoelectrode materials are TiO_2, WO_3, Fe_2O_3, $BiVO_4$ SnO_2 and Cu_2O and their modifications [10,11,15–17]. Recently, nanostructured photoelectrodes showed radically improved properties. In fact, due to the small size of the nanocrystalline structures, the photogenerated carriers are always created near the surface, where water conversion takes place [9,18,19]. Nanostructured electrode materials can be used to address some of the intrinsic limitations of the materials: visible light absorption, efficient charge carrier separation and transport, interfacial charge-transfer kinetics, appropriate positions of the conduction and valence band energy levels with respect to the required reaction potentials, and good stability in contact with electrolytes under dark and light illumination conditions [10].

A photoelectrode-based system comprises two electrodes, an anode and a cathode, both immersed in an aqueous electrolyte solution; at least one of the electrodes must be photoactivated under illumination. When a semiconductor with the ideal set of properties is immersed in an electrolyte solution and illuminated, the correspondent photon energy is used for splitting water into hydrogen and oxygen [20]. Currently, there are different types of PEC reactors, most of them responding to the need of testing new photoelectrodes, but less attention is being given to the improvement of such devices in order to increase their overall performance. The photoreactors reported for PEC water splitting exhibit various shapes and configurations: e.g. simple cubic or cylindrical open vessels, closed vessels equipped with an ion exchange membrane separating hydrogen from oxygen evolutions [5], H-type PEC cells [6,21], sandwich assembly, among other more complex cells, such as the ones that allows tandem configurations (PV+PEC system in a single embodiment) [15,22] – Fig. 2. Among the typical PEC cells, more complex ones were also developed, such as the “Cappuccino” PEC cell [23] designed by the LPI group at EPFL (Switzerland) and the cell designed and built by the MECS group at TU Delft [10].

Still, to make this technology marketable, it is not only necessary to find new photoelectrode materials, but also to develop photoelectrochemical devices with an optimized design that allows reaching a commercial performance level. For this, a special attention was given to study the effect of the position of the electrodes towards each other and towards the light source. Two PEC cells' configurations were disclosed, always with the main concern of positioning the electrodes for maximizing the solar light harvesting: (i) transparent n- and p-type electrodes, facing each other (the bandgaps of the photoelectrodes are such that the light not absorbed in the first photoelectrode can be absorbed in the second one – in series arrangement) [24]; and (ii) n- and p-type photoelectrodes placed one beside the other such as both photoelectrodes face the same light source – in parallel arrangement [25]. Despite these works, nowadays only simple PEC reactor configurations are actually commercially available and

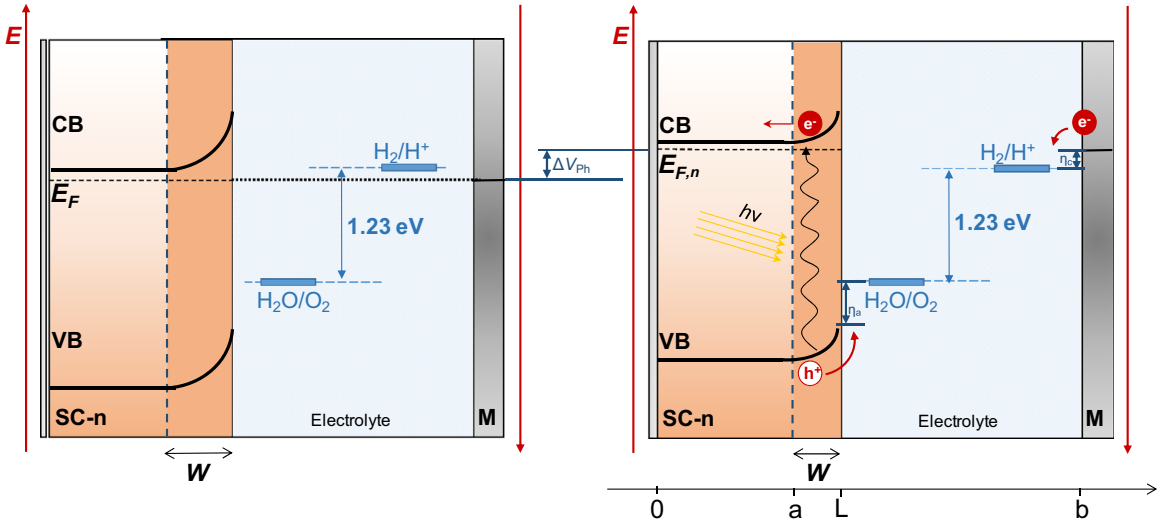

Fig. 1. Energetic diagram of a PEC cell under dark (a) and illumination (b) conditions.