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Towards the hydrogen production by photocatalysis

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ABSTRACT

Nowadays, problems derived from climate change urgently demand us to focus our attention on new alternatives to fossil fuels. Within this framework, the photocatalytic production of hydrogen as a clean fuel from oxygenates arises as a necessary option that must be considered. Thus, the development of highly efficient photocatalyst is crucial in order to achieve a viable technology under the industrial point of view. For this sake, it is necessary to understand the principles of photoreforming reaction. In this brief review we will revisit the different photocatalytic materials proposed in the literature highlighting on the role of different co-catalysts.

1. Introduction

In the early 1874, the visionary writer Jules Verne predicted that "*water will be the coal of the future*" in his science fiction tale "The Mistery Island". A century later, Fujishima and Honda could state in the lab the prediction made by Verne [1]. In this widely referenced experiment they showed that band gap excitation of anatase TiO_2 in a photoelectrochemical cell with a Pt counter electrode and an applied bias resulted in water splitting into hydrogen and oxygen. This scientific result has becoming the inspiring step in the development of a large studied field of the photocatalysis focusing on the water splitting reaction. Although the extensive research over the years in order to refine the process, nobody has come up with a system that is both efficient and inexpensive enough to produce sufficient hydrogen to be used as a clean-burning fuel on the roads, in industry, and at home.

The relevancy of this discovery is getting more evident taking into consideration the socioeconomical and environmental situation in the last decades. It is widely believed that hydrogen will play an important role in this global system since it is considered the ultimate clean energy carrier. Hydrogen can be produced from a variety of feedstocks. These include fossil resources, such as natural gas and coal, as well as renewable resources, such as biomass and water with input from renewable energy sources (e.g. sunlight, wind, wave or hydro-power). A variety of process technologies can be used, including chemical, biological, electrolytic, photolytic and thermo-chemical [2]. Each one is in a different stage of development, and offers unique opportunities, benefits and challenges. At present, H_2 is mainly produced from CO and CH_4 from fossil fuels by a steam reforming reaction which is accomplished by coupling with water gas shift and hydrogen purification reactions [3]. However, the forthcoming effective reduction of fossil fuel reserves as well as the serious environmental problems associated with CO_2 production has inspired the development of viable alternatives. Among these, the solar photocatalytic application for hydrogen production by photoreforming in which sunlight and water are used as the hydrogen source is a highly appreciated alternative [4]. In spite of these attractive particularities, the actual hydrogen production rates are still far from a practical application status. Thus, several reported works on high scale reactors indicated that the obtained H_2 productions are quite modest [5]. It is clear that the optimization of the photocatalytic system is crucial in order to make this attractive technology feasible under the industrial point of view.

In this sense, Rodríguez et al. recently showed that hydrogen generated from solar sources could be competitive with that obtained from non-renewables, and point towards design strategies that can significantly aid in the reduction of solar-fuels production costs [6]. Similarly, Pinaud et al. clearly demonstrates that if technical progress is made to meet material performance targets and with appropriate plant-scale engineering, direct solar hydrogen produced by water splitting reaction can be produced at a cost which meets the US Department of Energy target threshold of \$2.00–\$4.00 per kg H_2 [7]. These authors performed an exhaustive analysis which revealed that improvement in the solar-to-hydrogen efficiency (STH, which correlates the hydrogen production rate and energy of incidence solar light) of the panel-based systems could substantially drive down their costs. For a

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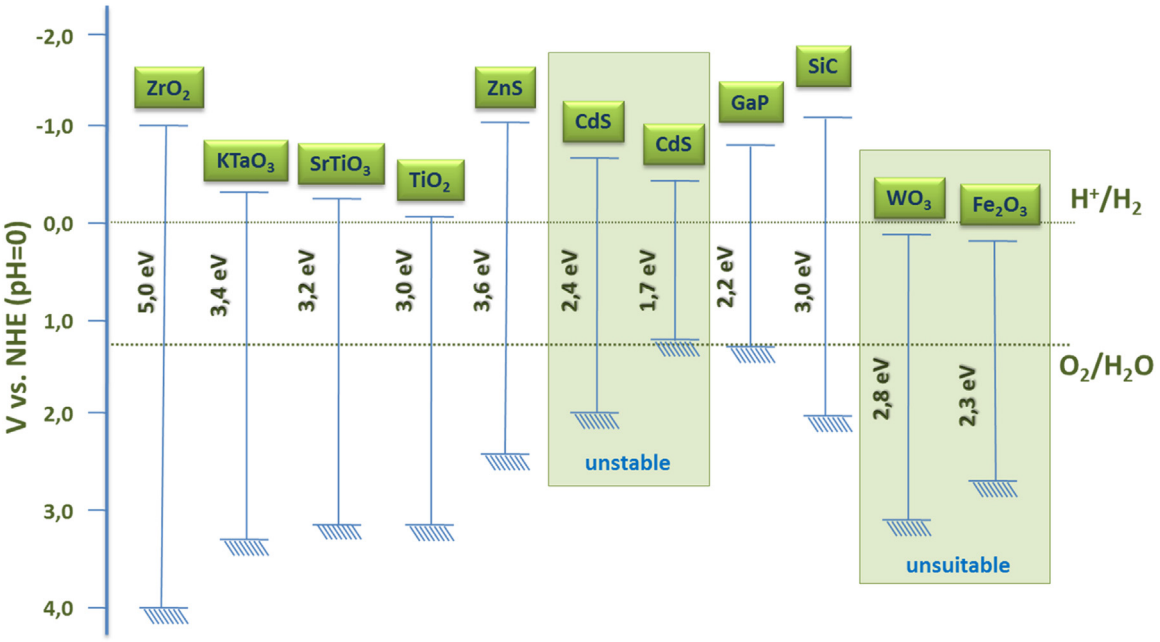

Fig. 1. Bandgaps and band edge positions of selected semiconductors in relation to the redox potentials for water splitting reaction.

given STH of 10% and a photocatalyst lifetime of ten years, the price of hydrogen was estimated to be $1.6 per kg, which could meet the mentioned target hydrogen price. In a recent perspective analysis, Domen et al. argued that due to the limitation of UV-active photocatalyst to increase the STH, it is necessary to develop and activate narrow-band-gap semiconducting photocatalysts for practical operation despite the present low activity of photocatalysts with absorption edge wavelengths longer than 600 nm for the overall water-splitting reaction [8]. These authors finally conclude that photocatalytic systems must be designed bearing scalability in mind.

Over the last three decades the overall photocatalytic water splitting process has been extensively studied pursuing to enhance the photoefficiency of the process [9]. However, the earliest research focused more on developing good photocatalysts than on actually understanding the process itself. Recent advances in the tailoring of new photocatalysts for solar water splitting pass through the comprehension of the band electronic structure which subsequently would lead to improvements using band engineering.

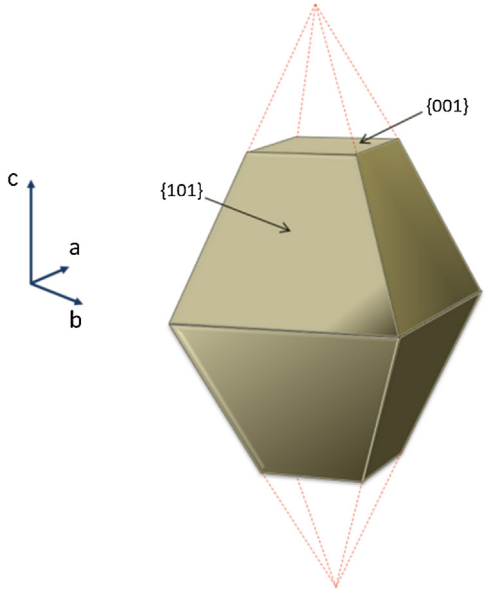

Fig. 2. Morphology of anatase nanocrystals.

2. General considerations on H_2 production reaction

From a thermodynamic point of view the water splitting reaction is energetically unfavoured process. Thus, water transformation into H_2 and O_2 is an uphill reaction which needs the standard Gibbs free energy change of 237 kJ/mol.

$$2\,H^+ + 2e^- \rightarrow H_2 \text{Hydrogenevolutionhalfreaction}$$

$$2OH^- + 2\,h^+ \rightarrow \tfrac{1}{2}O_2 + H_2O \text{Oxygenevolutionhalfreaction}$$

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \text{Overallwatersplitting}$$

The redox potentials for both reduction and oxidation processes determine the possible candidate photocatalyst by the positions of the valence and conduction bands and therefore strongly limit the range of possible photocatalysts. Both the reduction and oxidation potentials of water should lie within the band gap of the photocatalyst.

Regarding to the formal electronic structure of a potential photocatalyst for H_2 production, there are two important requirements to be accomplished: (i) The band gap should be 1.23 eV < Eg < 3.26 eV. (ii) The band positions should be located as follows: the bottom of the conduction band should be more negative than the redox potential of H^+/H_2 (0 V vs NHE) meanwhile the top of the valence band should be more positive than the redox potential of O_2/H_2O (1.23 V).

Thus, from a thermodynamic point of view the water splitting reaction should be easily achieved using a photoinduced catalytic process involving any materials which satisfy the above conditions. However, the overall photocatalytic water splitting reaction is an endothermic reaction. This means that, in order to overcome such an energy barrier, photons of higher energy are needed.

Within the great number of photoactive semiconductors proposed for water splitting ans photoreforming reactions, till now