INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 7247–7261

Available online at www.sciencedirect.com

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Review

Photocatalytic membrane reactors for hydrogen production from water

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ARTICLE INFO

Article history:
Received 7 November 2013
Received in revised form
21 February 2014
Accepted 28 February 2014
Available online 30 March 2014

Keywords:
Photocatalytic membrane reactors
Hydrogen production from water
Overall water splitting

ABSTRACT

Hydrogen is considered today a promising environmental friendly energy carrier for the next future, since it produces no air pollutants or greenhouse gases when it burns in air, and it possesses high energy capacity. In the last decades great attention has been devoted to hydrogen production from water splitting by photocatalysis. This technology appears very attractive thanks to the possibility to work under mild conditions producing no harmful by-products with the possibility to use renewable solar energy. Besides, it can be combined with the technology of membrane separations making the so-called photocatalytic membrane reactors (PMRs) where the chemical reaction, the recovery of the photocatalyst and the separation of products and/or intermediates simultaneously occur. In this work the basic principles of photocatalytic hydrogen generation from water splitting are reported, giving particular attention on the use of modified photocatalysts able to work under visible light irradiation. Several devices to achieve the photocatalytic hydrogen generation are presented focusing on the possibility to obtain pure hydrogen employing membrane systems and visible light irradiation. Although many efforts are still necessary to improve the performance of the process, membrane photoreactors seem to be promising for hydrogen production by overall water splitting in a cost-effective and environmentally sustainable way.

Introduction

Hydrogen is considered an ideal fuel for the next future. It does not produce any contaminant when it burns in air, it is a clean and a non-polluting energy carrier. It is the most common element on earth, mostly present in water, biomass and hydrocarbons. Nowadays, the most widely used industrial process for hydrogen production is the Steam Methane Reforming (SMR), which is also the most economical process [1]. This process involves many different catalytic steps, as long as natural gas (or methane) and hydrocarbon fuels that

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http://dx.doi.org/10.1016/j.ijhydene.2014.02.174
0360-3199/

remains at a low or moderate price. However, industrial hydrogen production results in equally large carbon dioxide emissions. Moreover, the emission of greenhouse gases also needs to be reduced to solve the problem of the global warming.

Other fuel processing technologies for hydrogen production are partial oxidation and autothermal reforming. Partial oxidation converts hydrocarbons to hydrogen by partially combusting the hydrocarbon with oxygen. The process requires high temperatures with some soot formation and the hydrogen/carbon oxide ratio from 1:1 to 2:1. Autothermal reforming is typically conducted at a lower pressure than partial oxidation reforming and has a low methane slip to atmosphere. However, these processes require an expensive and complex oxygen separation unit in order to feed pure oxygen to the reactor.

Fuel fossil burning, which contributes to the greenhouse gas pool, and also the eventual depletion of the world's fossil fuel reserves need for a development of cheap and very efficient new technologies. One strategy could be to apply steam reforming methods to alternative renewable materials [2–4] such as that ones from crops. Not only do these biomass-conversion schemes turn waste into a valuable product, but in addition, any carbon dioxide in the processes could be soaked up by planting new crops to provide the required biomass. A biomass strategy could represent a useful alternative to the current fossil fuel methods.

Solar and wind that are the two major sources of renewable energy, also represent a promising way for sustainable hydrogen production, although their cost still remains high. In the last years there has been a great interest of research in water splitting to make hydrogen using thermochemical, photobiological and photocatalytic systems. In thermochemical processes, heat from sunlight at around 2000 °C could be collected and used to carry out the water photodecomposition in presence of a semiconductor. The main drawback of this approach is the careful control of materials able to resist to heat, in addition to the high cost required to concentrate the solar light [5]. Photobiological water splitting is based on the use of oxygenic/anoxygenic photosynthetic microorganisms in anaerobic conditions. This technology could be an efficient method to generate hydrogen also from waste water but it still presents the problem of the carbon dioxide formation in the products when anoxygenic bacteria are used to promote the reaction. Hydrogen production by oxygenic bacteria currently offer more advantages because it leads to the decomposition of water into hydrogen and oxygen, but it also has many difficulties especially for the scale-up and the low hydrogen yield. Water electrolysis could become a useful alternative for producing clean hydrogen. It is essentially the conversion of electrical energy to chemical energy in the hydrogen form, with oxygen as useful by-product [6]. The most common electrolysis technology is alkaline based, but the research is developing also in proton exchange membrane processes and solid oxide electrolysis cells units. Currently, electrolysis is more expensive than using large-scale fuel processing techniques to produce hydrogen. It can become more competitive as the cost continues to decrease with the technology advancement. Alternatively, photocatalytic water splitting using semiconductors could offer a promising way for low cost and environmentally friendly hydrogen generation from solar energy [7–19].

In the last decade photocatalysis has become more and more attractive for the research in water splitting to produce hydrogen and oxygen using clean and renewable sources, for organic synthesis and for purification of water and air with benefit for environment and for the industry regarding the development of technologies. Compared with traditional advanced oxidation processes the technology of photocatalysis is known to have some advantages, such as easy setup and operation at ambient temperatures, no need for post-processes, low consumption of energy and consequently low costs.

Increasing attention has being taken to recently developed photocatalytic membrane reactors (PMRs), devices which combine a photocatalytic process with a membrane separation to obtain chemical transformations [20]. PMRs improves the potentialities of classical photoreactors (PRs) and those of membrane processes [21–23] with a synergy of both technologies thus minimizing environmental and economical impacts [24]. The membrane permits continuous operation in systems in which the recovery of the photocatalyst, the reaction and the products separation simultaneously occur. Higher energy efficiency, modularity and easy scale-up are some other advantages of PMRs with respect to convectional PRs.

In this paper the basic principles of photocatalytic hydrogen generation are presented, focusing on the photocatalysts able to work under visible light irradiation. The main techniques to modify semiconductors and their applications in the photodecomposition of water are reviewed. The development of membrane reactors able to work under visible light irradiation for the pure hydrogen generation is reported.

Basics principles of photocatalytic hydrogen generation

Heterogeneous photocatalysis was defined by Palmisano and Sclafani [25] in 1997 as "a catalytic process during which one or more reaction steps occur by means of electron–hole pairs photogenerated on the surface of semiconducting materials illuminated by light of suitable energy". As a direct consequence of this definition, both catalyst and light are necessary to induce a chemical process. In fact, upon irradiation excited states of the photocatalyst are generated and initiate subsequent processes like reduction–oxidation reactions and molecular transformations. The basic mechanism of heterogeneous photocatalysis have been investigated by many research groups [26,27] and can be summarized by the Fig. 1.

The irradiation of a semiconductor with light of energy equal or higher than its band gap energy (E_g) gives rise to promotion of electrons (e^-) from the valence band to the conduction band, leaving at the same time positive holes (h^+) in the valence band. The photogenerated electron–hole pairs can induce redox reactions with electron donor (D in Fig. 1) and electron acceptor (A in Fig. 1) adsorbed on the