Applied Catalysis A, General 550 (2018) 122–141

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Feature Article

Recent developments in the design of photoreactors for solar energy conversion from water splitting and CO_2 reduction

Van-Huy Nguyen[a,b], Jeffrey C.S. Wu[c,*]

[a] Department for Management of Science and Technology Development, Ton Duc Thang University, Ho Chi Minh City, Vietnam
[b] Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam
[c] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Keywords:
Photoreactor
Solar energy
H_2
Water splitting
CO_2 reduction
CO_2 hydrogenation

ABSTRACT

In recent decades, increasing interest has been devoted to improving the methods for solar energy conversion using water splitting and CO_2 reduction for solar fuel development. Herein, we discuss the historical background, present the current status, and expose development prospects to summarize and highlight the design of photoreactors. First, we discuss how converting CO_2 greenhouse gas to renewable fuels by using sustainable sunlight energy can simultaneously solve the problems of global warming and sustainable energy shortage. Several types of photoreactors for photocatalytic CO_2 reduction and CO_2 hydrogenation for realizing solar fuels have been developed extensively. Among them, an optical-fiber photoreactor, a monolith photoreactor, and an internally illuminated monolith photoreactor have received considerable attention recently. Second, we show how the design of novel twin photoreactor systems has great potential for solar energy conversion from water splitting. Combining water splitting and CO_2 hydrogenation to mimic photosynthesis is expected to play an important role in the future. Third, we demonstrate how a twin photoreactor also offers a new approach to producing solar fuels and simultaneously degrading organic wastewater. We believe that effectively combining H_2 production to hydrogenate CO_2 and organic wastewater treatment is a promising green technology. Finally, we propose critical challenges and prospects for the design of photoreactors. This review highlights the need to give more attention to the design of photoreactors for solar energy conversion from water splitting and CO_2 reduction.

1. Introduction

Currently, climate change and energy shortage are some of the greatest challenges for humanity [1]. Climate change is likely to alter several aspects of life worldwide; for example, it can affect human health and quality of life, plant and animal populations, communities, and biodiversity [2]. Notably, the warmest temperatures on record are the average global temperatures of the most recent years. This has been linked to the increasing levels of CO_2 and other major greenhouse gases (methane, nitrous oxide, and fluorinated gases) in the atmosphere due to recent human activity. Energy shortage is another heavily discussed topic as well. Fossil fuels, which currently provide nearly 87% of the global energy consumption, have a limit on their exploitation [3]. However, the world energy demand is increasing much more rapidly than the capacity of fossil fuels, leading to a current stage of energy shortage. The use of fossil fuels has a significant adverse impact on the environment and is considered a critical cause of global climate change. Therefore, the need to develop alternative energy sources is becoming increasingly urgent for sustainable economic growth [4]. Because CO_2 is one of the most abundant and economical carbon-containing sources, using this raw material as a potential building block for the development of alternative energy has received increasing attention [5]. Scientists are confident that converting CO_2 waste gas pollution into substitute fuels and simultaneously reducing atmospheric CO_2 levels by using renewable solar energy to drive photocatalytic reactions could provide a viable solution. This approach could answer both the rising energy demands and the need to reduce CO_2 emissions. However, the efficiency of this process is still relatively low [6]. Notably, the annual solar energy supplied to the Earth is 3×10^{24} J, which is approximately 10,000 times higher than the current total energy consumption worldwide [7]. In addition, many challenges remain to harvest this large energy reservoir. By 2030, solar photovoltaics and concentrated solar power are forecast to produce less than 1% of the global energy [1].

In our group, we promote solar energy by focusing on photocatalysis, including the stability of photocatalysts, operating conditions, and photoreactor design. One approach is to produce H_2 by photocatalytic water splitting. For this, two types of reaction could be

* Corresponding author.
E-mail addresses: nguyenvanhuy@tdt.edu.vn (V.-H. Nguyen), cswu@ntu.edu.tw (J.C.S. Wu).

https://doi.org/10.1016/j.apcata.2017.11.002
Received 1 August 2017; Received in revised form 29 October 2017; Accepted 2 November 2017

considered: (1) photoelectrochemical (PEC) and (2) photochemical (PC) reactions. For a PEC reaction, the photocatalyst is deposited as a thin film on a substrate to form a photoanode (or photoelectrode) for carrying out the water splitting reaction. The best advantage of a PEC cell is that water oxidation and reduction occur at different sites (electrodes), resulting in the simultaneous separation of evolved O_2 and H_2. This technique not only avoids the backward reaction of water splitting but also saves the cost of additional hydrogen separation before use. A PC reaction is another attractive reaction type that is used in conventional single reactors for producing hydrogen through photocatalytic water splitting. Compared with a PEC reaction, a PC reaction offers many advantages including no requirement for an electrical connection and an effective photocatalyst surface area that can be easily increased [8]. Many developed photocatalysts efficiently function with UV and visible light; these include: TiO_2 [8–10], $SrTiO_3$ [11], $CaTiO_3$ perovskite [12], layered structure $K_4Nb_6O_{17}$ [11,13], alkali-metal titanates $M_2Ti_nO_{2n+1}$ (M = Na, K, Rb, and n = 2, 3, 4, 6) [14,15], $M_2Ti_6O_{13}$ (M = Na, K, Rb, Cs) [16], ion-exchangeable layered perovskite-type oxides $A_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ (A= K, Rb, Cs; x = 0, 0.5, 1.0) [17], highly donor-doped (110) layered perovskite materials $A_mB_mO_{3m+2}$ (m = 4, 5; A = Ca, Sr, La; B = Nb, Ti) [18], alkali tantalates $ATaO_3$ (A = Li, Na, and K) [19], oxysulfides $Ln_2Ti_2S_2O_5$ (Ln = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er) [20], solid solutions of $ZnGeN_2$ and ZnO $(Zn_{1+x}Ge)(N_2O_x)$ [21,22], crystallized thin-wall Ta_3N_5 structures [23], Pt/$SrTiO_3$:Rh and WO_3 [24], and Pt/$SrTiO_3$:Rh and $BiVO_4$ [25]. In another approach, we focus on converting CO_2 greenhouse gas to renewable fuels by reducing and hydrogenating CO_2. Except for the reactants feeding (CO_2, H_2, and H_2O) and the photocatalyst system, there is no significant difference in the design with photoreactors for H_2 production and CO_2 reduction. Various photocatalysts for the solar-activated photocatalytic reduction/hydrogenation of CO_2 have been developed, such as plasmon-shaped AgX:Ag nanoparticles (X = Cl, Br) [26], TiO_2-based photocatalysts [27–31], Ti-oxide/zeolite [32], $ALa_4Ti_4O_{15}$ loaded with a layered perovskite Ag co-catalyst (A = Ca, Sr, and Ba) photocatalysts [33], hybrid CuO-$TiO_{2-x}N_x$ hollow nanocubes [34], and Ti_2CO_2 MXene [35]. However, in addition to the photocatalyst, different reactor types might affect the yield and distribution of the products [36]. Kim et al. reported that a fluidized bed and a slurry-type reactor showed more effective CO_2 conversions and hydrocarbon selectivity than a fixed bed reactor [37]. Lee et al. demonstrated that inadequate reactor design generates coke deposit from secondary reactions [38]. Obviously, photoreactors are integral to the photocatalysis process and constitute an important engineering factor. Some key parameters determine the types of photoreactors, such as the phases involved (single phase (gas, liquid), multiphase (gas-liquid, gas-solid, liquid-solid, gas-liquid-solid)), the mode of hydrodynamic operation (batch, semibatch, or continuous), the mixing and flow characteristics (completely mixed, some back-mixing, plug flow, nonideal flow characteristics), the geometric configuration (dimensions and shape), the light source specifications (output power, spectral distribution, shape, dimensions, operating and maintenance requirements), and the radiation source configuration relative to the reaction space [39,40]. Therefore, it is necessary to understand and design a suitable reactor, to find the best operating conditions for high selectivity. Among several factors, the enhancement of light harvesting, reduction of photon losses, and improvement product separation and charge carrier recombination are mainly considered in the design of a more effective photoreactor.

We review the research advances made in the design and development of photoreactors for solar energy conversion from water splitting and CO_2 reduction. Different photoreactor configurations affecting the yield and distribution of products are discussed. These photocatalytic reactions are potential candidate technologies for converting solar energy into hydrogen and hydrocarbons.

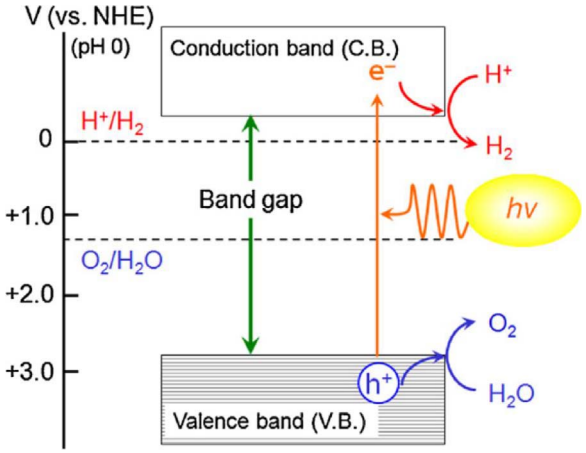

Fig. 1. Basic mechanism of overall water splitting on a semiconductor particle. (Reprinted from K. Maeda, K. Domen/J. Phys. Chem. C 111 (2007) 7851.).

2. Photocatalytic water splitting for hydrogen production

Hydrogen (H_2) has attracted increasing attention as an ideal alternative to fossil fuels due to its clean and highly efficient energy conversion. Although hydrogen is one of the most abundant elements on Earth, molecular hydrogen gas H_2 represents less than 1% [41]. The ideal cleanest means of producing hydrogen is to capture the energy that is freely available from sunlight and transfer it into valuable fuels such as hydrogen. Among the techniques of hydrogen production through solar water splitting (thermochemical, photobiological, and photocatalytic water splitting), photocatalytic water splitting shows the most potential [42]. This technique provides several advantages, such as reasonable efficiency, low cost, product (hydrogen and oxygen) separation during the reaction, and scalability suitable for household applications.

The principle of overall water splitting on a semiconductor particle is schematically depicted in Fig. 1. First, electrons (e^-) in the valence band are excited into the conduction band, leaving holes (h^+) in the valence band resulting in the formation of e^- and h^+ pairs when the semiconductor photocatalyst is exposed to radiation with an energy equivalent to or greater than its band gap. Subsequently, the photogenerated e^- and h^+ pair can reduce and oxidize a chemical species on the surface of the photocatalyst, respectively. The original structure (or chemical composition) of the photocatalyst remains unchanged if equal numbers of the photogenerated e^- and h^+ are consumed by the chemical reaction and/or recombination [42]. To enable photocatalytic water splitting, both the conduction and the valence bands must satisfy the following requirements: (1) the bottom of the conduction band is more negative than the reduction potential of H^+ to H_2 (0 V vs. NHE at pH 0) and (2) the top of the valence band is more positive than the oxidation potential of H_2O to O_2 (1.23 V vs. NHE) [43].

Two reaction types can be used to produce hydrogen through photocatalytic water splitting: (1) PEC and (2) PC reactions.

Since its inception by Fujishima and Honda, the PEC reaction has received considerable attention [44–47]. We review the literature for hydrogen production through the PEC technique and summarize the results in Table 1 [44,46–52]. In this design, the photocatalyst is deposited on a substrate as a thin film to form a photoanode (or photoelectrode) to carry out the water-splitting reaction. The main advantage of a PEC cell is that the oxidation and reduction of water occur at different sites (electrodes), resulting in the simultaneous separation of evolved O_2 and H_2. This technique not only avoids the backward reaction of water splitting but also reduces the cost of additional hydrogen separation. Among photoelectrode, TiO_2 shows high activity with an apparent quantum yield of 10.0% for water splitting [44]. Based on this property, the benefit of a PEC cell, which is called an H-