Journal of CO_2 Utilization 26 (2018) 98–122

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

A critical review on TiO_2 based photocatalytic CO_2 reduction system: Strategies to improve efficiency

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A R T I C L E I N F O

Keywords:
Photocatalytic CO_2 reduction
Thermodynamic
Mass transfer
TiO_2
Graphene

A B S T R A C T

The massive burning of fossil fuels to fulfill the augmenting energy demands of world have triggered the ever-increasing emission of carbon dioxide (CO_2); the main cause of global warming. Photocatalytic reduction of CO_2 into solar fuels and chemicals using everlasting solar energy seems promising technology to contemporaneously curb the globa1 warming and partially fulfill the energy requirements. This study focused on understanding the main challenges in photocatalytic CO_2 reduction systems and strategies to improve the efficiency of solar fuels production. The overview of fundamentals and latest developments in titania (TiO_2) based photocatalytic CO_2 reduction systems have been discussed. More specifically, thermodynamics, mass transfer, selectivity and reaction mechanism of photocatalytic CO_2 reduction are critically deliberated. In the main stream, developments have been categorized as strategies to enhance the different aspects such as visible light response, charge separation, CO_2 adsorption and morphology of photo-catalysts for TiO_2 based photocatalytic CO_2 reduction systems. Different modification techniques to overcome the low efficiency by fabricating advance TiO_2 nanocomposites through surface modifications, doping of metals, non-metals and semiconductor are discussed. The challenges lingering on against achieving the higher photocatalytic conversion of CO_2 into solar fuels are also investigated. In conclusion, brief perspectives and recommendations on the development of efficient photocatalysts are outlined which would be of vital importance for the improvements of conversion efficiency of CO_2 reduction system.

1. Introduction

Fast growing scientific developments are providing abundant conveniences to human society and instigating the profligate use of energy resources. It has been anticipated that the world energy demands may rise by 28% by 2040 [1]. Currently, most of the energy requirements are fulfilled by the combustion of fossil fuels such as coal, oil and natural gas [2] and if this trend persists, available fossil fuels reservoirs could be depleted in future [3]. Additionally, excessive combustion of fossil fuels is the main cause of global warming and threatening the ecosystem due to increasing level of greenhouse gas, CO_2. It has been anticipated that CO_2 level could reach to 750 ppm from its normal value of 400 ppm (0.04%) and global temperature may rise by 10–15 °F [4,5]. Hence, development of sustainable renewable energy resources is highly demanding to provide energy and control the global warming.

Several techniques have been utilized for the reduction of CO_2 such as carbon capturing and storage (CCS), electrochemical and thermochemical conversion, catalytic conversion, photoelectrochemical, biological fixation and photocatalytic reduction [6,7]. The CCS is extensively researched techniques with remarkable efficiency but environmental risk of leakage from geological storages, cost of compression and transportation have constrained its wide applications [8]. Similarly, electrochemical technique reduces CO_2 into value added chemicals using high power electrical energy, however, lower efficiency and electrode stability limit the process efficiency [9]. Likewise, the biological transformation of CO_2 into useful products by microalgae suffers from the limitations of production and regeneration of enzymes [10]. In addition, thermal and catalytic conversion of CO_2 into methane (CH_4) and carbon monoxide (CO) using transition metals catalysts is an efficient method for practical applications. Nevertheless, due to high temperature, pressure and exothermic reactions, capital and operational cost of process is high [11]. Photocatalytic technique, artificial

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https://doi.org/10.1016/j.jcou.2018.04.026
Received 23 November 2017; Received in revised form 24 April 2018; Accepted 28 April 2018
2212-9820/

photosynthesis, is the conversion of CO_2 and water into solar fuels like CH_4, CO, methanol (CH_3OH), formic acid (HCOOH) and formaldehyde (HCHO) under solar light irradiations. Among them, photocatalytic CO_2 reduction is the best process due to economical reactant (water), abundantly available solar energy, no toxic product or residue, and zero carbon emission [12]. Therefore, solar fuel generation from CO_2 through artificial photosynthesis process seems to be the most economical and eco-friendly approach for sustainable development.

Since first report by Inove and Fujishima et al. [13], intense efforts have been done to enhance the efficiency of photocatalytic CO_2 reduction. Various photocatalysts including zinc oxide (ZnO) [14], tungsten oxide (WO_3) [15], gallium phosphide (GaP) [16], gallium oxide (Ga_2O_3) [17], zirconium oxide (ZrO_2) [18], zinc sulfide (ZnS) [19], cadmium sulfide (CdS) [19], bismuth sulfide (Bi_2S_3) [20], lead selenide (PbSe) [21], graphitic carbon nitride (g-C_3N_4) [22] and titanium dioxide (TiO_2) [23] have been employed for photocatalytic degradation of CO_2. Among all, TiO_2 is broadly studied photocatalyst due to its unique properties, high chemical stability, availability and non-toxicity. Nevertheless, TiO_2 shows good activity under UV light irradiations and suffers from surface charge recombination problem [24–26]. Several strategies have been employed to enhance the performance of TiO_2-based photocatalysts such as surface modifications, heterojunction, doping with metals and non-metals, surface plasmons, morphologies, and other techniques to enhance the uptake of CO_2 [27–31]. Besides limitations of photocatalyst, fundamentals aspects such as reaction mechanism, selectivity of solar products, mass transfer and thermodynamics of photocatalytic CO_2 reduction are not well established.

The objective of this study is to summarize the current progress on TiO_2-based photocatalytic CO_2 reduction system. Fundamentals aspects such as thermodynamics, mass transfer, selectivity and reaction mechanism of CO_2 reduction are critically deliberated and illustrated with examples from other research studies. In the main stream, various strategies that have been reported to overcome the problems of TiO_2-based photocatalysts like photosensitizations, doping with metals and non-metals, heterojunctions, surface plasmons, novel architectures, functionalized surfaces, and state of the art morphologies have been analyzed and elaborated. Great emphasis has been devoted to the graphene modified TiO_2 composites due to peculiar features of graphene. Particularly, role of the graphene as a supporting material, electron acceptor, electron mediator in Z-scheme structures, surface plasmons of graphene, bandgap reduction, high surface area and delocalized π -conjugated electornic structure have been discussed and illustrated in detail. At the end, outlook of photocatalytic reduction of CO_2 along with new directions have been presented.

2. Fundamentals of CO_2 reduction

2.1. Principle of photocatalysis

Generally, photocatalysts are semiconductor materials in which excited electrons move from valence band (VB) to the conduction band (CB). The potential difference between the CB and VB is called bandgap energy [27]. Based on bandgap energy, semiconductors are categorized into two types; i) direct bandgap and ii) indirect bandgap semiconductors [29]. In direct bandgap semiconductor, minimum energy level of CB and maximum energy level of VB have same angular momentum position whereas indirect bandgap semiconductors possess different angular momentum [29]. Photocatalysis is the integrated reaction system involving principles of physical chemistry as well as photochemistry. When semiconductor surface is exposed to light irradiations with energy > bandgap of a semiconductor, electrons-holes pairs are generated. These electrons and holes carry out various redox reactions to generate final product [24,32,33]. However, if electrons and holes are not instantly depleted, they may recombine and lose their energy as illustrated in Fig. 1(a). Depending upon the electronic configuration of semiconductor, electrons and holes could undergo bulk or surface recombination. There could be two possible reasons for the electrons-holes recombination i) very small band gap energy where electrons can easily pair-up with holes and ii) electrons and holes fail to find the substrate and recombine due to a infinitesimal lifetime of nanoseconds [34,35]. As illustrated in Fig. 1(b), working of photocatalysis comprise of following steps; a) generation of an electron-hole pairs, b) transportation of electrons and holes to the surface of the photocatalyst, c) adsorption of the reactants on the surface and d) redox reaction e) formation of final products and desorption of products [34,36].

2.2. Thermodynamics of photocatalytic reduction of CO_2

Thermodynamics of photocatalysis can be discussed in term of temperature, light, CB and VB of semiconductor. Generally, a semiconductor may have completely filled VB and partially filled or empty CB. Forbidden energy level between VB and CB is called bandgap energy (E_g) and energy levels of atoms have different population of electrons (holes). When a semiconductor is exposed to the light with energy > E_g, it disturbs the population of electrons and holes in CB and VB, respectively. Electrons likely to achieve internal equilibrium within energy level rather than across bandgap because relaxation time with in conduction band is shorter than across the bandgap as shown in Fig. 2(a) [37–39]. States of electrons with internal equilibrium are called quasi equilibrium states and potential of electrons and holes in quasi-fermi levels are given by Eqs. (1) and (2) [40];

$$F_n = E_c + k_B T \ln \frac{n}{N_c} \tag{1}$$

$$F_p = E_v + k_B T \ln \frac{P}{N_v} \tag{2}$$

$$\Delta G = -|F_n - F_p| = -E_g - k_B T \ln \frac{np}{N_v N_c} \tag{3}$$

where E_C and E_V are CB minimum and VB maximum energy level positions, k_B= Boltzmann constant, N_c and N_v are effective densities of states in CB and VB, n and p are carrier's concentration.

Thermodynamic deriving force to trigger the photoreaction is directly proportional to the difference in populations of electrons and holes i.e., splitting value of ($|F_n - F_p|$). When semiconductor is at thermal equilibrium ($\Delta H = 0$), ΔG becomes zero resulting zero net force to derive photocatalytic reaction which implies that heat is not deriving force for the generation of electrons-holes pairs. Thus, for photocatalysis, energy of reaction is Gibbs free energy (ΔG) supplied by light irradiations to derive photoreaction Apart from mathematical discussion, experimental evidence has been reported by executing the photocatalytic CO_2 reduction reaction under dark, without photocatalyst and isotopic experiments [41,42] Hence, it can be stated that heat cannot induce the photocatalysis phenomenon. Conversely, it has been observed that yield of photocatalytic CO_2 reduction system increases with temperature [43]. Actually, temperature promotes the desorption of products from the surface of catalyst which enhances photocatalytic CO_2 reduction yield [44]. Hence, higher temperature is favorable in photocatalysis to speed up the rate of reaction.

Now considering light irradiations the only element to trigger photocatalysis, when a semiconductor is exposed to light, it leads to excitation and generation of electrons-holes pairs. Thermodynamics evidence of photocatalytic reaction via light can be outline using free energy of system as illustrated in Fig. 2(a). Free energy of system at ground state/dark, G_{dark} is less than free energy of system under light excitation, G_{light}. Additionally, chemical potential of electrons in quasi fermi level is higher than chemical potential of holes and it makes the overall ΔG positive. Light irradiations provide require ΔG and initiate the propagation of photoreaction at normal temperatures. From above discussion, it can be concluded that thermodynamic of photocatalysis can be clarified via free energy of system using light irradiations.