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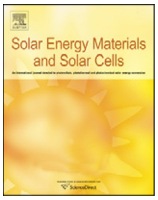

Review

Engineering TiO_2 nanomaterials for CO_2 conversion/solar fuels

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ABSTRACT

Global warming and fuel crisis have attracted attention to using carbon dioxide (CO_2) as a feedstock for preparing value-added compounds. Of particular interest in this context, we aim to review current knowledge of photocatalytic conversion of CO_2 towards solar fuels over titanium dioxide (TiO_2) from nanoengineering point of view. The basic principle of photocatalytic synthesis is briefly described, and then engineering design of the TiO_2 photocatalysts is emphasized with respect to reaction parameters. The links between photocatalytic properties of nanostructured TiO_2 and CO_2 conversion by using solar energy are addressed. Meanwhile, rationally orienting nanostructured TiO_2 in chemical reactors for CO_2 conversion and its prospects are highlighted for further development.

Contents

1. Introduction

The perceived risk of running out of conventional fossil fuels and the pollution risks associated with burning fuels led to crash programs in developing renewable energy [1–3]. Currently, much effort has been focused on developing sustainable electricity. A more challenging target is to produce fuels by using solar energy [4,5]. Solar fuel is an often used term indicating synthetic fuels derived from biomass through the biomass-to-liquid process. Solar energy and CO_2 are captured by plants and converted to complex molecules, which are then used as feed for a gasification process to produce final biofuels [4–6]. Compared to photovoltaic and wind energy, solar fuel generation delivers high-quality energy in the form of electricity, which has the advantage of solving the problem with temporal variations in supply as the final fuels are easy to store, and are compatible with the present transport sector. However, the efficiency of plants converting solar energy into chemical energy is typically lower than 1%, and its processing to biofuel is complex [4,6]. Therefore, it is necessary

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to simplify the process, enabling the possibility of efficient synthesis of fuels from sunlight, water and carbon dioxide.

A variety of research strategies have been devoted to explore viable routes towards the challenges, typically, bio-mimicking, thermochemical and low temperature photocatalytic conversion techniques. In bio-mimicking approaches as artificial photosynthetic systems or bioH_2 produced from algae and cyanobacteria systems, the conversion efficiency of special algae is up to $\sim$10% now, but the general issue is the complexity, high cost and lack of robustness [6–8]. Thermochemical approaches of CO_2 and H_2O dissociation inherently operate at high temperatures, which creates a number of issues in terms of materials and stability, cost-effectiveness and productivity [9,10]. Low temperature photocatalytic conversion by using proper semiconductors is an interesting option, but their conversion rate is still unsatisfactory [11,12]. The process is energy intensive and useful only if a renewable energy source can be used for the purpose [9,13,14]. Coupling the latter two routes, solar-driven catalytic conversion of CO_2 is a possible avenue to fuel generation at high rates.

Semiconductor materials such as TiO_2, ZnO, ZrO_2, CdS, Fe_2O_3, SiC, WO_3 and various combinations have been applied for photocatalytic conversion of CO_2. Considering the commercial availability, suitable optical/electronic qualities and chemical stability, TiO_2 nano-materials appears to be a distinguishing candidate [12,15]. Since photocatalytic reducduction of CO_2 to formic acid, formaldehyde, methanol, and methane over TiO_2 under UV light was discovered [16], many techniques have been applied to investigate suitable sensitizers for visible-light adsorption and to increase the activity of the reaction. A breakthrough in the photocatalytic reduction of gas phase CO_2 under solar radiation has been achieved by using doped TiO_2 nanotube (TNT) arrays [17,18]. Despite extensive research and progress, photocatalytic conversion of CO_2 over TiO_2 is still far from practical application due to the low yields of products.

Recently, a series of excellent reviews have been published on solar fuels [2–6,12,19]. The most advanced technologies and fundamental theories are summarized in details in Refs. [2–4,6]. In particular, titania materials as an interesting catalyst have been analyzed from surface chemistry point of view, and titania nanotubes show promising potential for the purpose [12,19]. To accelerate the innovation path on CO_2 conversion/solar fuels, we review the pioneering technologies with respect to TiO_2 assisted CO_2-reduction. The main focus of this article is on the accumulated knowledge of engineering TiO_2 nanomaterials and reactors for CO_2 conversion. Extensive literatures on the principle of TiO_2 photocatalysis, engineering TiO_2 catalysts, reaction parameters for reactor configurations are discussed. The links between catalytic properties of nanostructured TiO_2 and CO_2 conversion by using solar energy are highlighted.

2. Basic principle of photocatalytic synthesis

2.1. Photoexcitation and recombination

Basic principle of photocatalysis by using TiO_2 semiconductors to promote chemical redox reactions is discussed in this section. The reaction is initiated when a photoexcited electron (e^-) is excited from filled valence band (VB) to empty conduction band (CB) as absorbed photon energy, $h\nu$, equals or exceeds band gap of the semiconductor photocatalyst, leaving behind a hole in the VB. Thus, electrons and holes pairs are generated [3,20], as illustrated in Fig. 1 and Eq. (1).

$$TiO_2 + h\nu \rightarrow h^+ + e^- \tag{1}$$

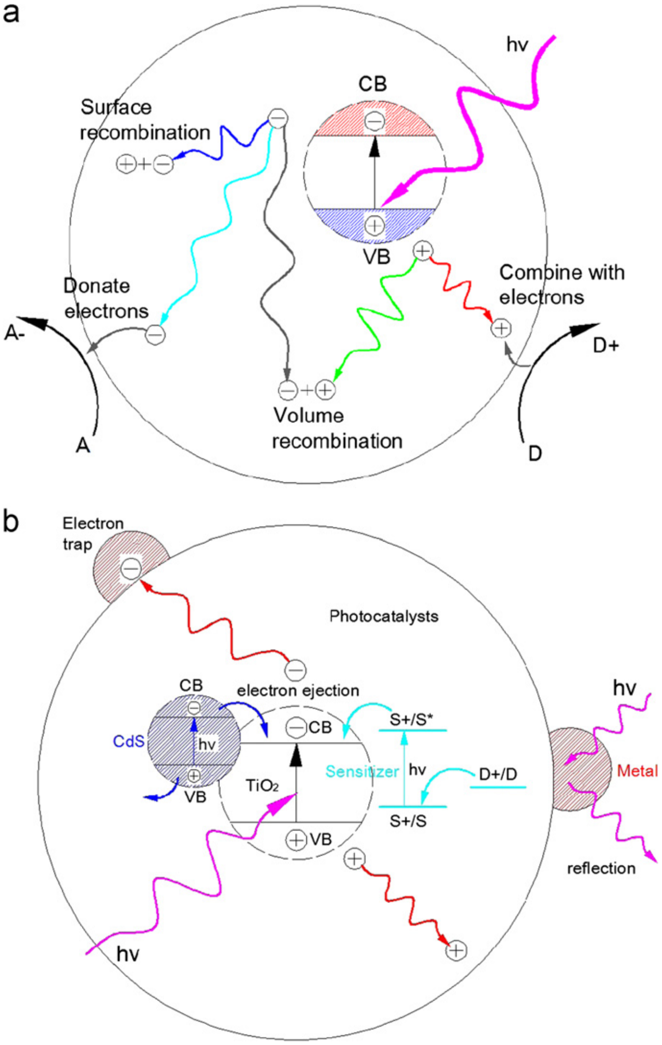

Fig. 1. (a) Schematic representation of band-gap formation and the electron-transfer process, (b) typical approaches for band-gap engineering: metal doping, dye sensitized and composite semiconductor.

The generated electrons and holes experience intraband transitions, migrate to surface and get trapped at the trap sites or they recombine radiatively or non-radiatively, as one of the several pathways. The rate of charge transfer depends on band edge position of the band gap and redox potential of the adsorbate species. When electrons migrate to the surface and after they are trapped at the edge of the CB, they serve as reduction centers, the semiconductor donates electrons to acceptors. Similarly, the holes being trapped at the VB edges serve as oxidizing sites where they combine with electrons from donor species [20,22]. However, recombination of electrons and holes prevents them from transferring to the surface to react with absorbed species, and the recombination occurs within the volume of the semiconductor or on the surface of the semiconductor [22]. Thus, suppressing the recombination is a crucial step in controlling the reactions for higher yields. It can be achieved by charge separation associated with the formation of a Schottky barrier, which is seen when photocatalysts are loaded with metals [20,23]. When the metals contact with the semiconductor catalyst, the electrons populate on metals if the Fermi level of the metal is lower than the CB edge of the semiconductor. So metals act as charge-carrier traps, resulting in an increase in the lifetimes of charge carriers. The details of engineering band gap for light harvesting and electron transport are discussed in Section 3.2.