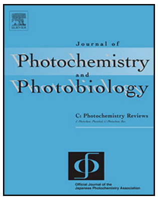
Journal of Photochemistry and Photobiology C: Photochemistry Reviews 18 (2014) 32–49

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology C: Photochemistry Reviews

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



Invited Review

Ion-exchangeable semiconductor materials for visible light-induced photocatalysis

Xu Zong, Lianzhou Wang*

ARC Centre of Excellence for Functional Nanomaterials, School of Chemical Engineering and AIBN, The University of Queensland, QLD 4072, Australia

ARTICLE INFO

Article history:
Received 19 June 2013
Received in revised form
23 September 2013
Accepted 4 October 2013
Available online 12 October 2013

Keywords:
Ion-exchangeable semiconductor
Band-gap engineering
Visible light-responsive
Photocatalysis
Water splitting

ABSTRACT

The use of semiconductor materials for solar fuel production and environmental remediation has attracted increasing attention in the past decades due to their potential to address important energy and environmental problems. Ion-exchangeable semiconductor materials represent one family of promising materials due to their unique crystal structures and structure-related photocatalytic activity. However, most of the ion-exchangeable semiconductor materials can only absorb UV light due to their wide band-gap. To efficiently utilize solar energy, it is indispensable to develop visible light-responsive semiconductor materials which can efficiently absorb solar electromagnetic radiation reaching the Earth's surface. In this review article, we summarize the recent advances on ion-exchangeable semiconductor materials as visible light-responsive photocatalysts with particular focus on the band-gap engineering strategies and their photocatalytic applications.

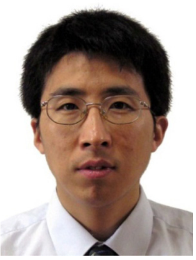
Contents

Abbreviations: LDH, Layered Double Hydroxide; 2D, two-dimensional; VBM, valence band maximum; DFT, Density functional theory; DOS, densities of states; PDOS, Partial densities of states; QDs, quantum dots; TBAOH, tetrabutylammonium hydroxide; TEOA, triethanolamine.

* Corresponding author. Tel.: +61 7 3365218; fax: +61 7 33654199.
E-mail address: l.wang@uq.edu.au (L. Wang).

1389-5567/$20.00 © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jphotochemrev.2013.10.001

Xu Zong received his PhD (2010) degree from Dalian Institute of Chemical Physics, Chinese Academy of Science. He is currently a postdoctoral research fellow in the ARC Centre of Excellence for Functional Nanomaterials (ARC-CFN), the University of Queensland. His research interests mainly focus on photocatalytic and photoelectrochemical water splitting using semiconductor materials, including ion-exchangeable layered materials.



Lianzhou Wang received his PhD degree from Shanghai Institute of Ceramics, Chinese Academy of Sciences in 1999. He is currently a Professor in School of Chemical Engineering and Research Director of ARC Centre of Excellence for Functional Nanomaterials (ARCCFN), the University of Queensland. His research interests include the design and development of functional nanomaterials for use in renewable energy conversion/storage systems, including photocatalysts, photoelectrodes for low cost solar cells, and rechargeable lithium ion batteries.

1. Introduction

1.1. Background and basic mechanism of photocatalysis

The increasing concern over the depletion of traditional fossil fuels and the serious environmental problems has re-triggered the passion on the utilization of solar energy at the turn of the new century. The main fascinating features afforded by solar energy are its abundance and cleanness. It is estimated that the magnitude of the available solar energy striking the earth's surface in 1 h (4.3×10^{20} J) is even higher than that consumed on the planet in 1 year (4.1×10^{20} J in 2001) [1]. Therefore, the capability of harvesting solar energy through a sustainable and cost-effective manner offers an ideal approach to satisfy the human's demand for renewable energy [2,3]. However, the huge gap between the actual utilization of solar energy and its enormous theoretical potential defines a compelling imperative to develop credible avenue of utilizing solar energy.

The conversion of solar energy via photocatalytic reactions that occur on the surface of semiconductor materials has been extensively investigated ever since the pioneer work of Fujishima and Honda on using TiO_2 photoanode for photochemical water splitting [4]. Up to now, several approaches such as photocatalytic and photoelectrochemical water splitting, solar cells, etc. have been proposed and developed to deposit solar energy into different energy forms such as H_2 fuel and electricity. Moreover, photocatalysis has been considered as a promising approach for the sustainable organic pollutants decomposition in water and air, which has been already used in some practical applications [5].

Regardless of the different reactions occur on the semiconductor surface, the basic mechanism for all the above-mentioned photocatalytic reactions is essentially the same. Fundamentally, photocatalytic reactions involve the following steps shown in Fig. 1: (1) Light energy is absorbed by the photocatalyst. If the incident light energy is equivalent to or higher than the band-gap of the semiconductor, electrons can receive energy from the photons and are excited from the valence band to the conduction band, leaving free holes in the valence band. (2) The photo-generated electrons and holes (charge carriers) may recombine either in bulk or on surface of semiconductor within a very short time, releasing energy in the form of heat or photons. However, if the electrons and holes are lucky enough, they could migrate to the surfaces of the semiconductor particles. (3) The free electrons can subsequently undergo reduction reactions with electron acceptors adsorbed by the surface of semiconductor, whereas the holes can directly oxidize adsorbed molecules or react with surface hydroxyl groups to produce hydroxyl radicals which are strong oxidizing agents. These oxidation and reduction processes together with some subsequent secondary reactions are the basic mechanisms of photocatalytic process, which underpin the development of a number of very important photocatalytic applications including organic pollutant decomposition (oxidation process by holes) for water and air purifications, water splitting and CO_2 conversion.

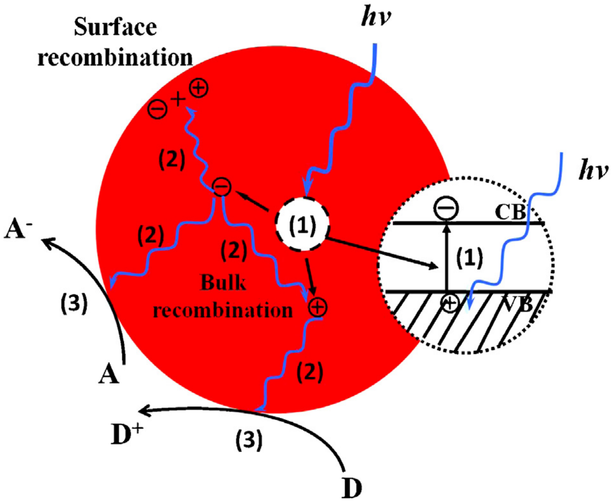


Fig. 1. Schematic steps for photocatalytic reactions that occur on semiconductor surface.

1.2. Ion-exchangeable semiconductor materials

As semiconductor materials are the most important component in a photocatalytic system, the development of cost-effective, non-toxic, and highly stable semiconductor materials has been the focus of investigation. Up to now, different material systems, such as oxide, sulfide, phosphide, nitride, oxynitride, oxysulfide have been developed for the conversion of solar energy [6]. Among all the materials under investigation, ion-exchangeable materials are of great interest due to their unique crystal structures and attractive photocatalytic performance.

Generally, there are two types of ion-exchangeable materials, oxide and hydroxide materials. Fig. 2a shows the schematic crystal structure of $Cs_{0.68}Ti_{1.83}O_4$ oxide. This representative material is typical of a lepidocrocite-type layered structure. Two layers of the network of TiO_6 octahedra sharing four edges are nested into a zigzag sheet as the structure unit of the layered titanate, and the zigzag sheets are separated by Cs^+ or hydrated proton as interlayer counter-ions. Fig. 2b shows the schematic crystal structure of brucite-like Layered Double Hydroxide (LDH) materials. LDH materials are composed of positively charged layers as the building block. The layers consist of two kinds of metals that typically have +2, +3, or +4 oxidation states, octahedrally surrounded by oxo bridges and hydroxyl groups. Negatively charged anions are located in the inter-gallery to compensate for the excess charges of the building layers. One of the most interesting features of these two types of materials is their exchangeable nature of the interlayer cations or anions, which facilitates the incorporation of functional foreign ions into the materials. More interestingly, through well-developed intercalation–exfoliation, appreciable number of these materials can be exfoliated into single-layer two-dimensional (2D) nanosheets, which can act as versatile building blocks for electronic,