Applied Surface Science 430 (2018) 53–107

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Graphene-based heterojunction photocatalysts

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ARTICLE INFO

Article history:
Received 21 June 2017
Received in revised form 16 August 2017
Accepted 28 August 2017
Available online 4 September 2017

Keywords:
Graphene
Heterojunction photocatalysts
Schottky junctions
Artificial photosynthesis
Z-scheme heterojunctions
Erath-abundant cocatalysts

ABSTRACT

Due to their unique physicochemical, optical and electrical properties, 2D semimetallic or semiconducting graphene has been extensively utilized to construct highly efficient heterojunction photocatalysts for driving a variety of redox reactions under proper light irradiation. In this review, we carefully addressed the fundamental mechanism of heterogeneous photocatalysis, fundamental properties and advantages of graphene in photocatalysis, and classification and comparison of graphene-based heterojunction photocatalysts. Subsequently, we thoroughly highlighted and discussed various graphene-based heterojunction photocatalysts, including Schottky junctions, Type-II heterojunctions, Z-scheme heterojunctions, Van der Waals heterostructures, in plane heterojunctions and multicomponent heterojunctions. Several important photocatalytic applications, such as photocatalytic water splitting (H_2 evolution and overall water splitting), degradation of pollutants, carbon dioxide reduction and bacteria disinfection, are also summarized. Through reviewing the important advances on this topic, it may inspire some new ideas for exploiting highly effective graphene-based heterojunction photocatalysts for a number of applications in photocatlysis and other fields, such as photovoltaic, (photo)electrocatalysis, lithium battery, fuel cell, supercapacitor and adsorption separation.

1. Introduction

Since the first reported photocatalytic production of H_2 from water in 1972 using TiO_2 [1], a variety of semiconductor materials have been developed for the renewable production of solar fuels [2–4]. The interesting heterogeneous photocatalysis, including the photocatalytic water splitting (i.e., water reduction and oxidation), degradation of pollutants and carbon dioxide reduction (artificial photosynthesis, AP), turns out to be one of the most appealing solutions for environmental and energy sustainability through directly harnessing solar energy. However, so far, no one semiconductor can meet all requirements for practical photocatalysis, such as a good photocatalyst must be efficient, stable, safe, cheap and visible [5]. Therefore, various possible strategies to enhance the overall photocatalytic effciency, including band structure engineering, micro/nano engineering [6], bionic engineering, co-catalyst engineering, surface and interface engineering, have been widely employed for engineering heterogeneous semiconductors.

Since the pioneering reports on the strong ambipolar electric field effect of semimetallic graphene by Geim and coworkers in 2004, graphene nanosheets, as a metal-free two-dimensional (2D) multifunctional nanoplatforms, have attracted extensive attention for electronic, catalytic and energy applications due to its unique electric, optical, structural and physiochemical properties [7]. Especially, many significant breakthroughs have been achieved for the large-scale synthesis of 2D graphene nanosheets through liquid-phase exfoliations. Interestingly, as a new class of emerging novel building blocks, 2D graphene nanosheets could also be used to fabricate various tailorable hybrid semiconductor nanomaterials with controllable compositions, sizes, size distributions, and morphologies. In particular, a number of novel nanostructured heterogeneous photocatalysts based on 2D graphene nanosheets have been developed in the past several years due to their favorable absorption of solar radiation, efficient separation of charge carriers, high surface areas and exposed reactive sites [2,8–10].

As is known, the overall photocatalytic efficiency is significantly hindered by the fast electron–hole recombination and low light utilization, which are governed by all material parameters,

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http://dx.doi.org/10.1016/j.apsusc.2017.08.194
0169-4332/

including chemical composition, physical dimension, interfacial and electronic properties. Thus, a fundamental understanding and deterministic control of these chemical, interfacial and structural factors will enable the scalable production of 2D graphene nanosheet-based composite photocatalysts with the best photocatalytic behavior, which will be favorable for creating some robust composite systems for practical photocatalytic applications and fundamental insights into low-dimensional physics and chemistry at the single-atom level. Although some excellent reviews about 2D graphene nanosheet-based photocatalysis have been published in the past eight years [2,7–17], most of these reviews only focus on the diversified roles of graphene in the graphene-based photocatalysts, such as photoelectron mediator and acceptor, enhancing the adsorption capacity, tuning the light absorption range and intensity, photothermal effect and the macromolecular photosensitizer. More importantly, it has also been pointed that the photocatalytic performances of graphene-based composite semiconductors could be enhanced through improving the electronic conductivity of GR, strengthening the interfacial contact between GR and semiconductors, and optimizing the entire system of GR–semiconductorcomposites [2,12,13,18,19]. Clearly, the interfaces between graphene and semiconductors play the crucial roles in achieving the significantly boosted photocatalytic efficiency. However, so far, there has been no one systematic review about summarizing the multi-functional graphene-based heterojunctions for various applications of heterogeneous photocatalysis. It is generally regarded that constructing the heterojunction photocatalysts has been extensively shown to be capable of promoting the spatial separation of photogenerated electron–hole pairs through combining the advantages of integrated functional components, thus fulfilling the higher overall photocatalytic activity [20–25]. Thus, it is timely to comprehensively summarize the significant advances in the utilization of graphene-based heterojunction semiconductors and solar energy for heterogeneous photocatalysis. In this review, important graphene-based heterojunctions such as Schottky-junctions, Type-II heterojunctions, Z-scheme heterojunctions (including indirect and direct), Van der Waals heterostructures and In plane heterojunctions, will be thoroughly highlighted and discussed. We believe that this review will not only promote the further developments of new graphene-based heterojunction semiconductors and architectures with improved solar-to-chemical energy conversion efficiency for solar fuel production and storage, but also make positive contributions to utilize renewable solar energy for a sustainable environmental and energy future. Importantly, this review will facilitate the development of new materials and architectures for photovoltaic and sensing devices.

2. Fundamental of graphene-based heterojunction photocatalysts

2.1. Fundamental mechanism of heterogeneous photocatalysis

To date, it is well accepted that, during photocatalytic reactions, the photogenerated electrons and holes in the excited semiconductors could accomplish the conversion of solar energy into chemical energy through complex multi-step processes, which are generally composed of the following seven typical processes (Fig. 1), (1) the photoexcitation of charge carriers, the transfer of holes (2) and electrons (3) to the semiconductor surface, the recombination of electon/hole pairs in the bulk (4) and on the surface (5) of semiconductor, and surface oxidation (6) and reduction (7) reactions, respectively [2,5–7,26,27]. Apart from these above kinetics processes, the fundamental thermodynamic requirements for a given photocatlytic reaction must be satisfied. The detailed thermodynamic requirements for photocatalytic dye degradation/bacteria disinfection, CO_2 reduction and hydrogen production have been discussed in other papers, which were summarized in Fig. 2. Clearly, the single-electron/multi-electron O_2 reduction reaction (ORR) and water oxidation reaction (WOR) are crucial for the photocatalytic dye degradation/bacteria disinfection (as observed in Fig. 2), whereas multi-electron CO_2 reduction reaction (CRR), H_2 evolution reaction (HER) and O_2 evolution reaction (OER) play vital roles in achieving the photocatalytic production of solar fuels [4,6,7]. According to the relative positions between CB levels of semiconductors and redox potentials of specific reactions, some commonly-used photocatlysts could be classified into three types: strongly oxidative semiconductors with much higher VB levels for WOR, strongly reductive semiconductors with much higher CB levels for CRR and HER, semiconductors with moderate oxidation and reduction ability [6]. The detailed band positions and potential applications of some typical photocatalysts are summarized in Fig. 3. As shown in Fig. 3, it is obvious that Fe_2O_3, WO_3 and $BiVO_4$ are the excellent visible-light-driven semiconductors for driven the oxidation reactions, whereas CdS, g-C_3N_4, Cu_2O and SiC are the promising semiconductors for achieving the production of solar fuels under visible light irradiation [28–31]. For the latter, their photo-generated electrons with higher reduction potentials could also readily migrate to the graphene with higher work function to drive various reduction reactions, thus leading to their extensive application of the corresponding semiconductor/graphene composites in the different photocatlytic fields, which will be further highlighted in the following sections.

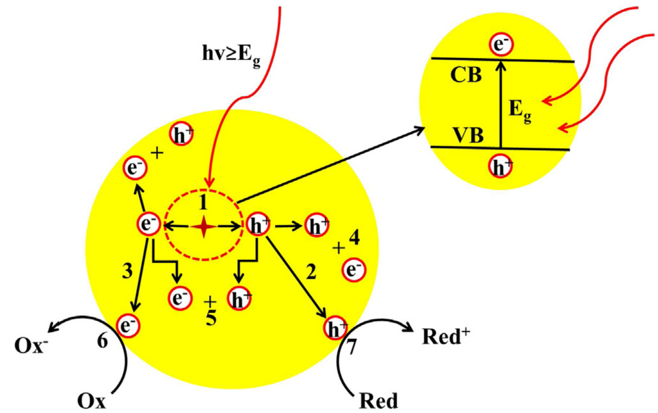

Fig. 1. Typical processes during the semiconductor photocatalysis, (1) the photoexcitation of charge carriers, the transfer of holes (2) and electrons (3) to the semiconductor surface, the recombination of electon/hole pairs in the bulk (4) and on the surface (5) of semiconductor, and surface oxidation (6) and reduction (7) reactions.

To improve these above kinetic processes and meet thermodynamic requirements, various engineering strategies have been extensively proposed in the past decades [5]. These engineering strategies could be divided into the thermodynamic and kinetic ones, which have been summarized in Fig. 4. Typically, thermodynamic strategies include the construction of wide spectrum responsive photocatalyst and modification of wide-band-gap semiconductors through proper composition engineering, whereas the challenging processes, such as charge separation, transport and utilization could be effectively boosted by exploiting high-efficiency charge-transfer nanostructures, high-quality heterojunction interfaces and highly reactive surface and cocatalysts, respectively [5,28,32–40]. Fortunately, all these strategies could be achieved by the multi-functional graphene [7]. Concretely speaking, graphene could not only be thermodynamically utilized in the construction of wide spectrum responsive photocatalyst or the doping of wide-band-gap semiconductors, but also kinetically improve the photocatalysis through fabricating high-efficiency charge-transfer