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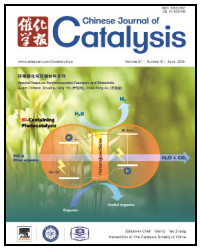

Review (Special Issue on Environmental Catalysis and Materials)

Recent advances in bismuth-containing photocatalysts with heterojunctions

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ABSTRACT

Photocatalysis has received much attention owing to current energy and environmental crises. The use of an appropriate photocatalyst is important to a photocatalytic process. The development of photocatalysts that absorb light over a wide range of wavelengths and efficiently separate charge carriers remains a challenge and hot research topic. With strong visible-light-absorption ability, bismuth-containing photocatalysts are of great interest to scientists. However, measures have to be taken to enhance the light absorption efficiency and to lessen the problem of the recombination of charge carriers. Known approaches are the formation of heterojunctions through (1) loading of a noble metal, (2) semiconductor combination, (3) metal and nonmetal doping, (4) carbon-based material modification, and (5) Bi metal loading. The present review summarizes recent advances in this respect. Finally, the future development and potential applications of bismuth-containing photocatalysts with heterojunctions are briefly discussed.

1. Introduction

Photocatalysis is regarded as the most promising technique for solving the problems of energy shortages and environmental pollution, which threaten the future development of human society. Photocatalytic technology has bright prospects in areas such as the generation of clean hydrogen by water splitting, CO_2 reduction into useful organics, and organic synthesis under mild conditions. Furthermore, the photocatalytic decomposition of organic and/or inorganic pollutants into CO_2, H_2O and nontoxic products without secondary pollutants has been considered a potential method of environmental remediation [1–6].

Since Fujishima and co-workers reported TiO_2 as a photocatalyst for H_2 and O_2 generation from water splitting [7], much attention has been paid to TiO_2 and TiO_2-based photocatalysts [8,9]. However, with a wide band gap of 3.2 eV, TiO_2 can only be excited under ultraviolet irradiation and it uses less than 4% of solar energy. Much effort has thus been made to improve the visible light absorption ability of TiO_2; such efforts include noble metal loading, element doping and combining TiO_2 with semiconductors having narrow band gaps. Meanwhile, achievements have been made in the development of novel photocatalysts driven by visible light. Among novel photocatalysts, bismuth-containing photocatalysts have received tremendous attention, and their advancement has been summarized systematically by Yu and co-workers [10]. They presented the types of bismuth-containing photocatalysts and discussed the effects of the preparation method, structure, morphology, and composition on photocatalytic properties. Despite

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much effort, a practically viable photocatalyst that is cheap and possesses sufficient efficiency and stability is yet to be found. Indeed, it is difficult to simultaneously fulfill the different metrics with a single material.

The recombination of photogenerated electrons and holes goes against the photocatalytic process. Since Li and coworkers first reported the high separation efficiency of charge carriers over heterojunction photocatalysts [11,12], there has been much similar research [13–15]. It is generally regarded that the drawbacks of single-component photocatalysts can be eliminated through the synthesis of a heterogeneous photocatalyst of integrated functional components that combines the advantages of the individual components. In this article, we present a wide range of heterojunctions fabricated to enhance the performance of bismuth-containing photocatalysts. The heterojunctions are noble metal/Bi-containing composite, semiconductor/Bi-containing composite, heterojunctions between two Bi-containing photocatalysts, carbon-based material/Bi-containing composite, and Bi metal/Bi-containing semiconductor. Finally, we briefly discuss the future development and potential applications of this class of photocatalysts.

2. Bismuth-containing photocatalysts loaded with a noble metal (Schottky junction)

With excellent conductivity and strong electron trapping ability, noble metals are used in photocatalysis for the separation and transfer of light-excited charge carriers. Under visible light, the transfer of charge carriers between the noble metal and support (semiconductor) can follow two pathways. In one case, the support of a wide band gap cannot be excited under visible-light irradiation but there is a transfer of electrons from the surface plasmon of the noble metal. In the other case, which is normally observed, there is a transfer of excited electrons from the semiconductor to noble metal. Furthermore, the noble metal of nanostructures can induce surface plasmon resonance (SPR), which can broaden the light absorption range of a composite photocatalyst [16]. In recent years, noble metals have been widely used as cocatalysts to enhance photocatalytic activity, especially in the areas of water splitting and the selective oxidation of organics.

As reported by Manna et al. [17], because of lattice similarity between Au and Bi_2S_3, a junction forms between the (101) plane of Au and (221) plane of Bi_2S_3. With the formation of heterojunctions, the light absorption is red-shifted and the SPR peak of Au broadens from ca. 520 to 560 nm (Fig. 1(a) and (b)). When photocatalytic reduction of methylene blue (MB) under visible-light irradiation (500-nm monochromatic light) is used as a probe reaction, the transfer of photogenerated electrons observed over the Au-Bi_2S_3 heterojunctions is much faster than that over Au or Bi_2S_3. The Au-Bi_2S_3 photocatalyst is typically nanostructured, and the improvement in photocatalytic activity can be attributed to the enhanced separation of charge carriers and the broadened light absorption range as a result of the noble metal plasmon (Fig. 1(c) and (d)). Owing to the fast electron transfer from the semiconductor to noble metal, Pt-coupled Bi_2WO_6 composite shows highly selective and efficient conversion of aromatic alcohols to their corresponding

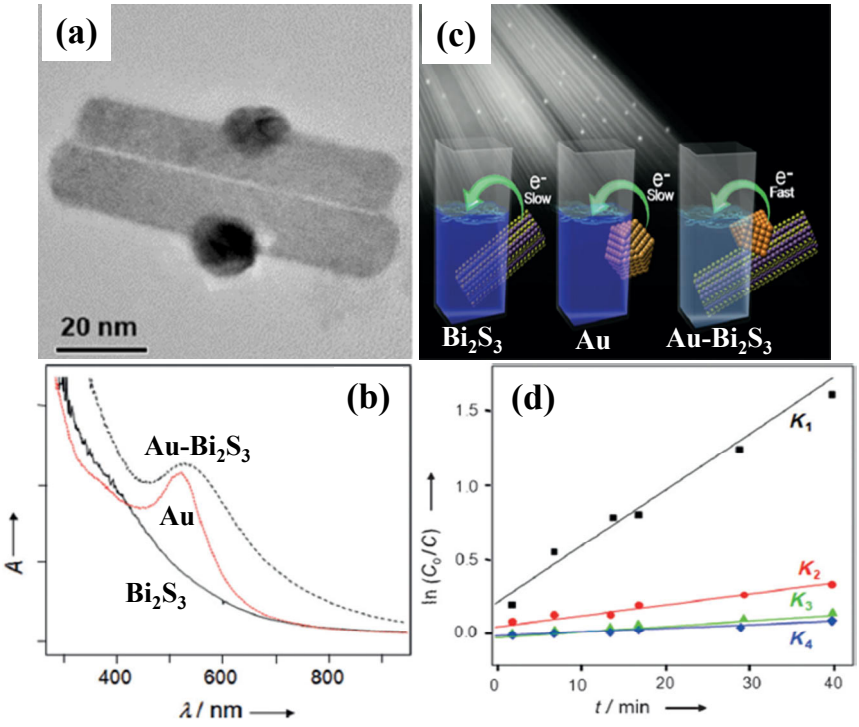

Fig. 1. (a) Transmission electron microscopy image of the Au-Bi_2S_3 heterostructure. (b) Light absorption spectra of Bi_2S_3 rods, Au nanoparticles and Au-Bi_2S_3 heterostructures. (c) Schematic of the favorable photoreduction of MB. (d) Rate of dye degradation with irradiation progress controlled under different conditions. The samples were irradiated using a Xe lamp with a wavelength of 500 nm. k_1 (0.037 min^{-1}), k_2 (0.007 min^{-1}), k_3 (0.004 min^{-1}), and k_4 (0.002 min^{-1}) denote the dye-degradation rate constants when Au-Bi_2S_3, a mixture of Au and Bi_2S_3, Bi_2S_3, and Au were used as catalyst, respectively [17].