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Photocatalytic degradation of butyric acid over Cu_2O/Bi_2WO_6 composites for simultaneous production of alkanes and hydrogen gas under UV irradiation

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ABSTRACT

In present study, photocatalytic production of alkanes and hydrogen gas from butyric acid solution over Cu_2O/Bi_2WO_6 composites has been investigated under UV irradiation. The Cu_2O/Bi_2WO_6 heterojunction composites were synthesized by a two-step method, first by a hydrothermal method, and then by a simple reduction precipitation method. The as-prepared samples were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), ultraviolet–visible diffuse reflection spectroscopy (DRS) and photoluminescence spectroscopy (PL). In Cu_2O/Bi_2WO_6 composites, the larger spherical Cu_2O were covered by smaller Bi_2WO_6 nanosheets. The 24.36 wt%Cu_2O/Bi_2WO_6 composite showed the highest photocatalytic activity for production of alkanes and hydrogen gas. The enhancement in photocatalytic activity can be ascribed to increment in light absorption and effective inhibition of recombination of photogenerated carriers at the heterostructure interface. Based on distributions of gaseous products and intermediates in liquid, a possible mechanism for photocatalytic decomposition of butyric acid over Cu_2O/Bi_2WO_6 composites is proposed. Our results provide a method for pollutants removal with simultaneous production of alkanes and hydrogen.

Introduction

Alkanes and hydrogen have been considered to be the most promising candidates as substitutes for fossil fuels [1]. Nowadays, both alkanes and hydrogen are mainly produced from fossil-based materials. However, the environmental concerns together with fast depletion of fossil fuels reserves are increasingly demanding clean and renewable energy sources. Hydrogen production via photocatalytic water-

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splitting process using solar light and semiconductors has been considered as one of the major strategies for solving the global energy and environmental problems due to its potential as a method for obtaining clean and highly efficient energy from abundant H_2O and renewable solar energy [2]. At present, the energy conversion efficiency of solar-to-hydrogen by semiconductors is too low for this technology to be economically sound. The main barriers are the rapid recombination of photogenerated electrons with holes as well as poor activation of semiconductors by visible light. In response to those deficiencies, one effective approach to prohibit rapid recombination of photogenerated electrons with holes is added organic compounds as electron donors, which react irreversibly with the photogenerated holes [3]. A large variety of organic compounds such as alcohols [4], organic acids [5], glucose [6], as well as some organic pollutants [7] have been selected as electron donors during photocatalytic H_2 production process. Another approach is how to develop photocatalysts with high activity in visible light region. Therefore, numerous efforts have been paid to prepare semiconductors such as CdS [8], Cu_2O [9], WO_3 [10], BiOX ($X = Cl$, Br, I) [11], $BiVO_4$ [12], Ag_3PO_4 [13], etc. and to explore their photocatalytic performances in visible light region at various laboratories.

In addition to hydrogen gas, simultaneous production of alkanes can also be achieved during photocatalytic water-splitting process when some short-chain aliphatic acids are used as electron donors. Kraeutler and Bard first discovered that methane and ethane could be obtained when photocatalytic degradation of acetic acid in the presence of Pt/TiO_2 under UV irradiation [14]. Recently, Mozia et al. reported that CH_4, C_2H_6, C_3H_8 and H_2 could be simultaneously produced when acetic acid was degraded over TiO_2 nanoparticles under UV illumination [15]. Heciak et al. found that simultaneous formation C_1–C_3 hydrocarbons and hydrogen were obtained when photocatalytic decomposition of acetic acid using Cu-modified TiO_2 photocatalyst [16]. Asal's group also reported that some hydrocarbons and hydrogen were simultaneously generated in acetic acid solution using lanthanide modified TiO_2 photocatalyst [17]. Mozia et al. reported that simultaneous generation of hydrocarbons and hydrogen gas from acetic acid over Fe-modified TiO_2 photocatalyst [18]. Mozia's group recently found that simultaneous production of alkanes and hydrogen could be fulfilled when other organic compounds such as methanol, ethanol and glucose were selected as electron donors during photocatalytic water-splitting process [19]. In the previous studies, our group found that acetic acid and propionic acid could be successfully converted to hydrogen gas during photocatalytic process using Pt/TiO_2 photocatalyst [20,21]. Compared with acetic acid and propionic acid, butyric acid is more difficult to degrade by microorganism. Therefore, there is a need to investigate the feasibility of converting butyric acid to alkanes and hydrogen by photocatalytic process. To our knowledge, there is no reports regarding photocatalytic production of alkanes and hydrogen when butyric acid was used as electron donors in the literature. In this regard, in the present research, Cu_2O/Bi_2WO_6 nanocomposites have been synthesized to explore their photocatalytic activity for production of alkanes and hydrogen gas from butyric acid.

Nowadays, bismuth-based materials have received intensive attention for their promising applications as active photocatalysts. Among the reported Bi-based semiconductors, Bi_2WO_6 is an n-type semiconductor with medium band gap (2.8 eV). Bi_2WO_6 is also one of the simplest Aurivillius oxides and has layered structure [22]. Its unique layered structure is favorable for charge transfer, thus retarding the recombination of photogenerated electrons with holes. In the last few years, Bi_2WO_6 with various morphologies such as microflower [23], nanoplate [24], nanocage [25], etc. have been fabricated by different methods to explore their photocatalytic activities for degradation of organic pollutants in the visible light region. However, the photocatalytic activity of Bi_2WO_6 alone is not desirable due to its quick recombination of photogenerated holes with electrons. To improve its photocatalytic activity, it is a good approach to couple Bi_2WO_6 with another p-type semiconductor. The p-n heterojunctions can be formed at the interface when an n-type semiconductor couples with another p-type semiconductor. The heterojunctions in composites can dominate photogenerated electron–hole pairs in the direction of transport, the distance of separation and the rate of recombination, leading to the efficient separation of photogenerated electron–hole pairs [26]. Cuprous oxide (Cu_2O) is a p-type semiconductor which has attracted interest in photocatalytic H_2 production due to its small band gap (2.0 eV), high photoactivity and low cost production. The Cu_2O/Bi_2WO_6 composites prepared by Liu et al. have revealed lower charge-transfer resistance, higher photocurrent intensity and outstanding photocatalytic activity for degradation of methylene blue [27]. To best of our knowledge, the information about photocatalytic activity of Cu_2O/Bi_2WO_6 composites for production of alkanes and hydrogen is limited in the literature. Thus, in the present work, the Cu_2O/Bi_2WO_6 composites have been fabricated to evaluate their photocatalytic activity for production of alkanes and hydrogen.

Biomass, the most versatile renewable resource, can be converted to hydrogen or biogas by biological process. Some organic wastes such as residuals of food processing plants, organic fraction of municipal solid waste and agricultural residues rich in carbohydrate content, can be used for production of H_2 or methane. In the previous studies, organic wastes such as food wastes [28], molasses [29], organic solid waste [30], municipal solid waste [31], etc. have been effectively converted to hydrogen gas by fermentative bacteria. During biological H_2 fermentation process, the distribution of liquor products depends on kinds of substrates, types of bacteria, operational factors and so on. In liquor solution, acetic acid, butyric acid, propionic acid, ethanol as well as methanol are usually identified as main by-products [32,33]. The challenge is how to utilize volatile fatty acids and alcohols produced by hydrogen fermentation effectively. Traditionally, the effluent containing mostly organic acids and alcohols is directly pumped to a bioreactor to convert the produced organic acids into methane and carbon dioxide [34,35]. Recently, the photo-fermentation process has been used to convert those organic acids into hydrogen gas by photosynthetic bacteria. Acetate, lactate, succinate and so on have been successfully converted to H_2 gas by photosynthetic bacteria at various laboratories [36–38]. However, propionic acid and butyric acid are more difficult to convert into hydrogen gas

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