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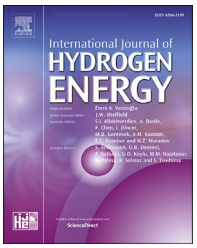

Enhanced photocatalytic hydrogen evolution using a novel in situ heterojunction yttrium-doped $Bi_4NbO_8Cl@Nb_2O_5$

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ABSTRACT

The novel in situ Z-scheme heterostructure materials Y-doped $Bi_4NbO_8Cl@Nb_2O_5$ ($Bi_{4-x}Y_xNbO_8Cl$, x = 0, 1, 1.33, 2, 2.67, 3) have been synthesized successfully via a solid-state method. The as-prepared samples were characterized by XRD, Raman spectrum, SEM, EDS, element mapping, HRTEM, XPS and UV–vis spectrum to explore the structures, morphologies and optical properties. Photocatalytic activities were evaluated for hydrogen generation using the Pt as the co-catalysts. HRTEM results indicated the Pt particles were deposited on the surface of the Bi_4NbO_8Cl. Photocatalytic activities were evaluated by hydrogen generation. While photocatalytic results showed that BiY_3NbO_8Cl composites exhibited the best performance of hydrogen production under the full-range irradiation ($\lambda > 300$ nm) while the Y-doped $Bi_4NbO_8Cl@Nb_2O_5$ with Y:Bi molar ratio 1:1 obtained the highest efficiency with ultraviolet light eliminated. The H_2 production was 1.35 mmol and 0.9 mmol in 8 h, respectively. Furthermore, a direct Z-scheme mechanism with enhanced hydrogen evolution competent for accelerating the separation of photogenerated carries has been presented and proved by electrochemical impedance spectroscopy (EIS). Finally, considering the conclusions of the electron spin-resonance spectroscopy (EPR), ·OH radicals served as an active species played an important role in the hydrogen production. Mechanisms about the action of the ·OH radicals were also proposed.

Introduction

Past decades have witnessed the increasingly extensive explorations focusing on TiO_2 as a promising photocatalyst due to its strong oxidizing ability, low toxicity, low cost, and facile synthesis since it was reported in 1972 [1]. However, TiO_2 also has its disadvantages, such as the rapid recombination of the photogenerated carries as well as unable to response to visible light, among the photocatalysis applications [2,3]. Recently, researchers have made their efforts to quest for novel materials, which can be applied for photocatalytic hydrogen evolution, with higher efficiency and activity than TiO_2. As a result, a majority of materials, like graphene [4], $Cd_{0.5}Zn_{0.5}S$

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[5], C_3N_4 [6], $Bi_{0.5}Y_{0.5}VO_4$ [7,8], $SrTiO_3$ [9], for photocatalytic hydrogen evolution have been explored.

The single layer Sillen-Aurivillius perovskite Bi_4MO_8X (M = V, Nb, Ta; X = F, Cl, Br, I), usually investigated as a series of ferroelectric materials, have ignited the interests of scientists who devoted themselves to photocatalytic water purification [10]. The structures of Bi_4MO_8X are composed of single-layer MO_4 perovskite blocks which are separated by $(Bi_2O_2)_2Cl$ blocks [11]. Several achievements have measured the photocatalytic activities of Bi_4MO_8X, especially on the removal of organic pollutants. In 2007 Huang's group valued the photocatalytic activity of the Bi_4NbO_8Cl by the degradation of methyl orange [10], afterwards, Bi_4NbO_8Br [12], Bi_4TaO_8Cl [13] and Bi_4TaO_8I [14] have been fabricated successfully via a solid state reaction method. To improve the photocatalytic performances on the removal of pollutants, hydrothermal method also has been utilized. Bi_4NbO_8Cl with a hierarchical nanostructure was synthesized by Swetha et al. The mineralization efficiency of 75% for Congo red dye can be achieved evaluated removal of the organic carbon in 80 min [15]. Hu and co-workers applied the Bi_4VO_8Cl to the degradation of aciclovir, levofloxacin, sulfonamide, adrenaline as well as ribavirin under visible light irradiation [16]. Results showed that all of the drugs can be removed completely during 10 h. Nevertheless, the applications of Bi_4MO_8X were mainly concentrated on the photodegradation of organic pollutants, especially dyes, until Abe's group, in a creative way, indicated that hydrogen can be generated when Bi_4NbO_8Cl was irradiated in the methanol aqueous under a Xe lamp [17]. Li and co-workers also found Bi_4TaO_8Cl can be used for hydrogen evolution under visible light, which made the Bi_4MO_8X to be a novel promising material for photocatalytic hydrogen evolution [18]. Methanol, which was selected as the sacrificial reagent for hydrogen production in the aforementioned two studies, also can be served as a kind of energy. It needs further research to explore whether utilizing methanol as sacrificial reagent is economically suitable or not. On the other hand, investigating the novel substitute agents which are inexpensive with better performance on the hydrogen generation is a possible method to solve the discussed problems.

Glucose, also used as the sacrificial agents in the photocatalytic hydrogen evolution [19–25], is one of the cheapest carbohydrates as it can be directly produced from cellulose. It is widely accepted that cellulose is one of the rich and sustainable biomass energies of the earth [26]. Quite apart from that, more importantly, glucose also appears in wastewaters from the factories as a contaminant, which is quite normal latterly due to the rapid development of the agro-food industrials [27]. Photocatalysis has potential to be one of the most significantly and promising strategies for hydrogen production due to its clean and inexpensive properties. To improve the photocatalytic efficiency and activity, constructing a direct solid-state Z-scheme heterojunction, which can decrease the recombination rate of the photogenerated electrons and holes, has been proved to be a possible method. Z-scheme photocatalytic systems provoked the interests of scientists due to it can solve the problem of the traditional Type II heterojunction [28], which has the same band alignment while with an opposite tendency of charge transfer. The photogenerated electrons, which existed on the semiconductor with lower conduction band position, will be coupled with the holes on another semiconductor of a higher valence band potential. Electrons and holes, meanwhile, can be preserved and still posses the redox ability on the two semiconductors, respectively. Meanwhile, efficient charge separation and strong redox ability can be acquired via the heterostructures of Z-scheme.

Y_2O_3 has a strong effect on density and grain shape as well as unable to absorb the light of wavelength between 230 nm and 800 nm [29,30]. Our previous achievements manifested that the hybridization on the orbital will be occurred when bismuth and yttrium constituted for the solid solution, which could be beneficial for elevating the CB position of the photocatalysts [7,8]. In the present work, the induced in situ direct solid-state Z-scheme heterojunction Y-doped $Bi_4NbO_8Cl@Nb_2O_5$ photocatalysts have been fabricated successfully through its inductive action. Photocatalytic activity evaluation showed that hydrogen can be collected via these photocatalysts from photoreforming of the glucose. It also can be concluded that Y-doped $Bi_4NbO_8Cl@Nb_2O_5$ with an in situ direct solid-state Z-scheme heterojunction structure was beneficial for hydrogen generation.

Experimental

Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3·5H_2O$), potassium chloride (KCl), bismuth trioxide (Bi_2O_3), yttrium oxide (Y_2O_3), niobium oxide (Nb_2O_5), anhydrous glucose ($C_6H_{12}O_6$) and chloroplatinic acid hexahydrate ($H_2PtCl_6·6H_2O$) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the reagents were analytic graded and used as received without further purification. Ultrapure water was also used all over the experiments.

Synthesis of photocatalysts

Typically, BiOCl was prepared via a hydrothermal method according to the previous report [31]. Then, 6 mmol BiOCl, 9 mmol Bi_2O_3 and 3 mmol Nb_2O_5 were mixed together. Being grinded for 15 min, the composites were transferred to the crucible with a cover. After it was calcinated for 24 h in the muffle furnace at 1073 K, Bi_4NbO_8Cl can be collected.

Yttrium-doped $Bi_4NbO_8Cl@Nb_2O_5$ ($Bi_{4-x}Y_xNbO_8Cl$) was synthesized by the same method except that different mole amounts of Bi_2O_3 were substituted by Y_2O_3. 6 mmol BiOCl, x mmol Y_2O_3 and (9-x) mmol Bi_2O_3 (x = 0, 3, 4, 6, 8, 9) as well as 3 mmol Nb_2O_5 were mixed together. The products were denoted as Bi_3YNbO_8Cl (Bi_3Y), $Bi_{2.67}Y_{1.33}NbO_8Cl$ ($Bi_{2.66}Y_{1.33}$), $Bi_2Y_2NbO_8Cl$ (Bi_2Y_2), $Bi_{1.33}Y_{2.67}NbO_8Cl$ ($Bi_{1.33}Y_{2.67}$), BiY_3NbO_8Cl (BiY_3), respectively.

Characterization

X-ray powder diffraction (XRD) analysis was recorded with a Bruker advanced D8 powder diffractometer with a Cu-Kα radiation source. The scan ranges were 10–80° with $0.02°s^{-1}$. The morphologies of the catalysts were observed on a

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