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Enhanced Z-scheme visible light photocatalytic hydrogen production over α-Bi_2O_3/CZS heterostructure

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ABSTRACT

Depletion of fossil fuels and associated environmental issues has drawn attention of researchers to renewable energy resources and photocatalytic hydrogen production is considered to be safe and applicable method to meet future energy demand. Herein, we have used α-Bi_2O_3 nanorods for loading CZS ($Cd_{0.5}Zn_{0.5}S$) to form a heterostructure for photocatalytic H_2 production. The α-Bi_2O_3/CZS heterostructure was characterized through TEM, Elemental Mapping, XRD and XPS analysis. The α-Bi_2O_3/CZS heterostructure shows photocatalytic H_2 production rate of 254.1 μmol h^{-1} with apparent quantum yield of 6.8% (λ = 420 nm). The enhanced photocatalytic performance was supported by transient photocurrent response curves and electrochemical impedance spectroscopy (EIS) results which suggest the efficient charge separation and electron mobility in α-Bi_2O_3/CZS heterostructure. The intimate contact formed between α-Bi_2O_3 nanorods and CZS nanoparticles responsible for the efficient flow of electrons following a Z-scheme pattern resulting in higher photocatalytic H_2 production. Moreover, the as-synthesized α-Bi_2O_3/CZS heterostructure shows negligible loss of activity after 4 consecutive recycling cycles. Our findings open new possibilities for the design of heterostructure based photocatalysts.

Introduction

The world energy consumption has been grown exponentially in the past few decades [1]. The depletion of fossil fuels and associated environmental hazards provide a daunting challenge to the researchers to look for clean energy resources. One renewable source of energy is sun which provides (10^{22} J) daily energy, enough to meet global demands [2]. Over the last decades, various strategies have been employed to harvest solar energy into electrical and chemical energy. Among which water splitting under solar light irradiation to generate H_2 have attracted much attention due to renewable feedstock and greenhouse gas free technology [3]. Since the pioneer work on water splitting under solar light in 1972, various approaches have been employed for photocatalytic hydrogen

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production [4]. Among which, photocatalytic H_2 production operating under ambient conditions using a photocatalyst and sacrificial agents is considered most attractive due to its large scale applicability [5] and better recyclability.

In the recent years a number of semiconductors (TiO_2, WO_3, ZnO, Fe_2O_3, $SrTiO_2$, CdS, ZnS) have been evaluated for the visible light driven hydrogen production. However, none of them were able to reach at optimum conditions as few depends upon precious metals as co-catalyst others have photo-corrosion and poor recyclability problems under visible light [6–11]. The bandgap of CdS is 2.4 eV, which is a suitable candidate for photocatalytic hydrogen production. However, the fast recombination of charge carrier and photo-corrosion ability of CdS greatly restrict its practical applications [12]. Some efforts have been made to reduce the photo-corrosion of CdS, either by loading the noble metal on its surface or incorporating the metal sulphides/oxide nanoparticles into the interlayer [13]. Some authors also suggested that photocatalytic properties and stability of CdS could be improved by mixing with wide band gap semiconductors such as ZnS [14]. The incorporation of ZnS in CdS has been considered an efficient way where the metal atoms are mutually substituted in the crystal lattice [15]. Previous reports have suggested the use of $Cd_{1-x}Zn_xS$ for efficient photocatalytic hydrogen production [16,17]. However, some of these materials either prepared at elevated temperatures or showed poor recyclability making practical implications difficult.

Moreover, the development of heterostructure by combining $Cd_{1-x}Zn_xS$ with other semiconductors is a promising way to boost the activity [18]. The formation of heterojunction by integrating two or more semiconductors with matched band energy can optimize the absorption of light, promote the separation of photogenerated electron and holes through creating a built-in electric field in the space-charge region, and hence enhance the photocatalytic hydrogen production [19]. This artificial Z-scheme photocatalytic water splitting to generate H_2 was inspired by natural photosynthesis, in which electrons chain between photosystem II (PSII) and photosystem I (PSI) [20]. Bard in 1979, introduced this photocatalytic system by combining two semiconductors [21]. Since then, numerous approaches have been made to exploit the solar light at its greatest extent [22].

Bismuth oxide (Bi_2O_3) have attracted considerable attention in the fields of photo-catalysis, gas sensors and fuel cells due to its unique properties like high bandgap, good photoconductivity, remarkable refractive index and photoluminescence [23–25]. Bi_2O_3 have also shown excellent photocatalytic activity for the dye degradation under visible light irradiation [26]. However, most of bismuth oxide's polymorphs are not able to reduce protons to produce hydrogen under visible light irradiation due to positive conduction band position compared to H^+/H_2 potential [27]. Therefore, in order to make Bi_2O_3 as efficient visible light exploiting photocatalyst, its properties and band gap has to be tuned by doping or coupling with other metal oxides. As the development of highly efficient, low-cost and noble-metal free photocatalyst which can promote the separation of photogenerated electron and holes are needed to realize real Pt-free photocatalysts. Herein, we propose to use α-Bi_2O_3 and CZS ($Cd_{0.5}Zn_{0.5}S$) to synthesize a heterostructure with an interface connection for direct Z-scheme electron transportation, as presented by Mirtchev et al. [28]. The heterostructure will overcome the lower conduction band position problem of Bi_2O_3 and develop an intimate contact with CZS to facilitate the charge separation and electron transfer for efficient photocatalytic hydrogen production. The overall goal is to increase higher photo-efficiencies for water splitting with hybrid catalytic systems. The synthesis approach adopted for α-Bi_2O_3/CZS heterostructure is also easy and simple in order to achieve desired results. The as-synthesized α-Bi_2O_3/CZS heterostructure was characterized in terms of their morphological, structural, composition and light-absorption properties. The prepared α-Bi_2O_3/CZS heterostructure was used as efficient photocatalyst for the photocatalytic hydrogen production.

Experimental

Chemicals

Bismuth(III) nitrate pentahydrate [$Bi(NO_3)_3 \cdot 5H_2O$], sodium hydroxide (NaOH), Zinc acetate [$Zn(OAc)_2$], cadmium acetate [$Cd(OAc)_2$], Sodium sulfide nonahydrate [$Na_2S \cdot 9H_2O$], sodium sulfite (Na_2SO_3) were purchased from Sinopharm Chemical Reagent Co. Ltd. and were used as received. All other chemical reagents were of analytical grade and used as received without further purification.

Characterization

The morphology of the particles was observed by scanning electron microscope (SEM, JSM 6700F, JEOL). Transmission electron microscopic (TEM) images and high-resolution transmission electron microscopic (HRTEM) images were carried out on a JEM-2100F field emission electron microscope at an accelerating voltage of 200 kV. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and EDX elemental mapping images were taken on a JEOL JEM-ARF200F atomic resolution analytical microscope. The X-ray powder diffraction (XRD) patterns of the products were performed on a Philips X'Pert Pro Super diffractometer with Cu-Kα radiation (λ = 1.54178 Å). The operation voltage was maintained at 40 kV and current at 200 mA, respectively. The X-ray photoelectron spectroscopy (XPS) was carried out on a PerkinElmer RBD upgraded PHI-5000C ESCA system. A Shimadzu spectrophotometer (Model 2501 PC) was used to record the UV–vis diffuse reflectance spectra of the samples in the region of 200–800 nm. The elemental analysis was also carried out on an inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, ELAN 6000).

Synthesis of α-Bi_2O_3 nanorods

In a typical synthesis, 2.4 g of bismuth nitrate was added into 100 mL of DI water to obtained 0.1 M solution. The obtained solution was stirred for an hour, afterwards the pH of the solution was raised to ~8 by the slow addition of 5 M NaOH solution. The resulting solution was stirred for 12 h to obtained a light-yellow precipitate. The precipitate was separated through

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