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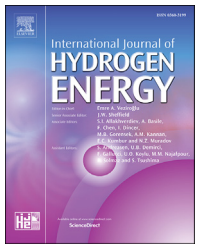

Highly efficient hydrogen evolution catalysis based on $MoS_2/CdS/TiO_2$ porous composites

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ABSTRACT

Efficient production of hydrogen through visible-light-driven water splitting mechanism using semiconductor-based composites has been identified as a promising strategy for converting light into clean H_2 fuel. However, researchers are facing lots of challenges such as light absorption and electron-hole pair recombination and so on. Here, new sheet-shaped MoS_2 and pyramid-shaped CdS *in-situ* co-grown on porous TiO_2 photocatalysts (MoS_2–CdS–TiO_2) are successfully obtained *via* mild sulfuration of MoO_3 and CdO coexisted inside porous TiO_2 monolith by a hydrothermal route. The scanning electron microscopy and transmission electron microscopy results exhibit that the MoS_2–CdS–TiO_2 composites have average pore size about 500 nm. The 3%MoS_2–10%CdS–TiO_2 demonstrated excellent photocatalytic activity and high stability for a hydrogen production with a high H_2-generation rate of 4146 μmol h^{-1} g^{-1} under visible light irradiation even without noble-metal co-catalysts. The super photocatalytic performance of the visible-light-driven hydrogen evolution is predominantly attributed to the synergistic effect. The conduction band of MoS_2 facilitates in transporting excited electrons from visible-light on CdS to the porous TiO_2 for catalytic hydrogen production, and holes to MoS_2 for inhibiting the photocorrosion of CdS, respectively, leading to enhancing the efficient separation of electrons and holes.

Introduction

In recent years, global environmental pollution and energy crisis has required the development of clean and reproducible energy as the substitute of traditional fuels [1]. Therefore, many of the research groups are trying for the conversion of solar energy to hydrogen fuel through artificial photocatalysts on the account of their cleanliness, environmental

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friendliness and potentially low cost [2]. Among efficient, earth-abundant, and sustainable H_2-producing photocatalysts, TiO_2-based photocatalysts have been received tremendous attention since the first report of H_2 generation through the photocatalytic water splitting on TiO_2 electrodes by Honda and Fujishima in 1972 [3]. Up to date, TiO_2 nanostructures have been considered to be promising photocatalysts owing to their superior physical and chemical properties including low cost, non-toxicity, abundance, high photostability, and easy synthesis [4,5]. However, anatase-crystallized TiO_2 nanostructures with the band gap of ca. 3.2 eV solely absorbs UV light of about 5% of the solar spectrum [6,7]. Furthermore, some drawbacks of TiO_2 photocatalysts such as their low quantum yield, low speed transfer of photo-excited electrons and holes, and high recombination rate of photo-generation carriers seriously prohibits their extensive applications of photodegradation pollutes and visible-light-driven H_2 evolution [8,9]. Therefore, various strategies have been used to modify the TiO_2 photocatalysts such as ion doping, noble metal deposition and sensitization with narrow bandgap semiconductors in order to enhance their photocatalytic activity [10–13].

Regarding the narrow-band-gap-semiconductor modification, metal chalcogenides have been deemed to be the good candidates for the photocatalytic H_2 production because of their appropriate band gaps [14–16]. Specifically, CdS nanostructures that have a relatively narrow band gap of 2.4 eV have been regarded as attractive visible light-driven H_2-production photocatalysts because of their visible light absorption ability and suitable conduction band edge position compared with H^+/H_2 normal chemical potential [17]. However, the efficient radiative recombination of photoexcited electrons and holes and the high kinetic barrier for hydrogen evolution over its surface sites do not allow the direct conversion of solar energy to hydrogen gas [18]. Hence, enormous studies have been performed on the CdS–TiO_2 composite photocatalysts. For instance, Cho et al. prepared self-assembled TiO_2 NTs decorated by CdS quantum dots, and the obtained products possessed obviously an enhanced photocatalytic activity [19]. Zhao et al. reported that CdS incorporated mesoporous TiO_2 exhibited high photocatalytic performance [20]. However, Such composites still suffer from some defects including low efficiency, quick recombination of photoexcited electron-hole pairs and photocorrosion, resulting in the low visible-light-driven H_2-producing efficiency. Therefore, it is necessary to improve the photocatalytic activity and stability for economic co-catalysts [21–23].

To date, experimental and computational results have shown that MoS_2 is a promising photocatalyst owing to its unique structure, narrow band gap, high thermal stability, low-cost and electrostatic integrity [24,25]. Particularly, stacked-layer MoS_2 frameworks sandwiched together in a graphite-like manner possess a good conductive behavior, properly preferred benefit to electrons and holes transportation [26]. Meanwhile, edge sites of MoS_2 are considered to be the active position for water activation to produce hydrogen under visible light irradiation [27]. In addition, the good conductivity of the single-layered MoS_2 could efficiently separate the electron-hole pairs, favoring the photocatalytic H_2-producing activity. Hence, MoS_2 has been widely utilized to incorporate into other semiconductor photocatalysts for improving the photocatalytic performance. For instance, Li et al. reported MoS_2/CdS heterojunction with the enhancement of photocatalytic activity compared to the noble metal doped CdS composites [28]. Min et al. synthesized MoS_2/CdS, showing obviously improved photocatalytic activity due to the matched energy bands of the heterostructure [29]. Liu et al. introduced the few-layer MoS_2 nanosheets and MoS_2 nanoparticles into TiO_2 nanobelts, respectively, and both of them demonstrated the enhanced photocatalytic activities [30]. On the basis of the reported results, multi-component nanocrystals exhibit multifunctional properties or synergistic performance for energy conversion and photoelectric catalysis applications.

Herein, we reported a new MoS_2–CdS–TiO_2 photocatalyst that was synthesized by a two-step method. It is highly expected that MoS_2 and CdS co-decorated TiO_2 can have high photocatalytic activity and stability. It is carefully designed that the pyramid-like CdS can extend the light absorption to the visible region to enhance hydrogen production efficiency and the layer-shaped MoS_2 can be acted as a conductive bridge to promote a transport of the photoexcited carriers to prevent the electron-pair recombination, and finally the porous TiO_2 can not only accept the electrons from the CdS conduction band due to the relatively positive electrode potential but also accelerate the electron transport speed to improve the light-driven hydrogen evolution. For the synthesis, it is simply designed that the porous MoO_3–CdO–TiO_2 can be prepared through a sol-gel method using the polystyrene (PS) as the template, followed by a calcination, and then, the porous sheet-shaped MoS_2 and pyramid-shaped CdS *in-situ* congested amongst porous TiO_2 photocatalysts can be hydrothermally synthesized *via* the sulfuration reaction of the porous MoO_3–CdO–TiO_2.

Experimental

Materials

$Cd(Ac)_2 \cdot 2H_2O$ (AR), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (AR), $K_2S_2O_8$ (AR), $NaHCO_3$ (AR), Na_2SO_3 (AR), Thiourea (AR), Tetrabutyl titanate (TBT, AR), Styrene (AR), alpha methyl acrylic acid (CP), absolute ethyl alcohol (AR) and ice acetate acid (AR) were purchased from Aladdin Industrial Corporation. And all chemical reagents were used without further purification.

In situ *synthesis of sheet-shaped* MoS_2 *and pyramid-shaped CdS congested among porous* TiO_2 *photocatalysts*

The MoS_2-CT samples were prepared using sol-gel method and calcination, respectively. Firstly, monodispersed polystyrene spheres (PS) with sizes of ~500 nm were prepared by the similar method reported previously [31]. Secondly, our new porous MoO_3–CdO–TiO_2 composites (hereinafter named as MoO_3-CT) were prepared according to the sol-gel method and followed by calcination at 450 °C temperature. Finally, the sheet-shaped MoS_2 and pyramid-shaped CdS congested among porous TiO_2 photocatalysts were synthesized through *in situ* sulfurizations by a hydrothermal method.