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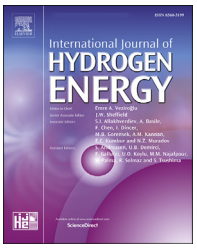

Novel polymer supported graphene and molybdenum sulfide as highly efficient cocatalyst for photocatalytic hydrogen evolution

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ABSTRACT

Exploiting photocatalysts with environmental friendliness, noble-metal-free and high efficiency is a great challenge for photocatalytic hydrogen evolution. In this work, we synthesized a novel MoS_2/rGO/$Cd_{0.6}Zn_{0.4}S$ composite catalyst based on microsphere-structural polymer with highly efficient photocatalytic activity under visible light irradiation. The 5.0%MoS_2/rGO/$Cd_{0.6}Zn_{0.4}S$ exhibited the highest H_2 evolution rate of 11.7 mmol/h/g, which about 2.1 times higher than that without MoS_2 and 4 times higher than that without PSGM. This superior photocatalytic activity, further demonstrated by the transient photocurrent responses and electrochemical impedance spectrum, was attributed to the effective separation of the photo-generated charge carriers promoted by the positive synergetic effect between the MoS_2 and graphene. This study provided a promising approach to achieve high-efficiency H_2 evolution based on graphene and MoS_2 without noble metals.

Introduction

Photocatalytic hydrogen evolution from water has been considered as a sustainable and viable method to solve the increasing global energy crisis and environmental problems [1–3]. Over the past few decades, extensive efforts have been devoted to finding suitable semiconductors as promising photocatalysts for H_2 production, such as TiO_2, CdS, ZnS, and C_3N_4 [4–10]. However, the low solar energy utilization and photocatalytic efficiency of most investigated semiconductor photocatalyst without noble metal cocatalysts are still the key limits for its large-scale industrial application [11,12]. Among various semiconductors, CdS was proven to be a promising candidate due to its high activity under visible light and suitable band gap energy for photocatalytic H_2 production under visible light. However, the fast recombination of photo-generated charge carriers and severe photocorrosion under long-term visible light irradiation of CdS restricted its application, tremendous efforts have been reported to overcome these drawbacks [13–15]. Fortunately, due to the improved stability, charge separation efficiency and controllable band structure, $Cd_{1-x}Zn_xS$ solid solutions might provide an opportunity to address the above problems during the photocatalytic

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H_2 production process [16–20]. For example, Zhou et al. demonstrated a one-pot hydrothermal approach to produce mesoporous $Cd_{1-x}Zn_xS$ solid solutions, which displayed large specific surface area and superior visible-light-driven H_2 production without any cocatalyst [21]. Actually, in recent years, solid solutions construction of sulfide semiconductors has made considerable achievements in the field of photocatalysis, however, satisfactory photocatalytic efficiency has not been achieved until now. Therefore, it is of great importance for developing new strategies in more efficient photocatalytic systems with earth abundant and inexpensive materials.

Thus, a novel carbon material has been attracted widespread attention, graphene, two-dimensional sheet of sp^2-hybridized carbon, which has high electron conductivity and large theoretical specific surface area. The fabrication of composite catalysts with graphene not only accelerate the interfacial electron transfer from photocatalysts to cocatalyst but also provide large specific surface area for the dispersion of the cocatalyst [22–28]. Recently, Huang [29] successfully fabricated a series of sulfide/graphene 3D nanospherical photocatalysts, the $Cd_{0.5}Zn_{0.5}S$/rGO showed excellent photocatalytic activities and it took about 30 min for completely degrades methyl orange under visible light. Their study found that enhanced photocatalytic activity of $Cd_{0.5}Zn_{0.5}S$/rGO sample was mainly due to rGO served as an electron mediator that greatly accelerate the separation of photon-generated carriers by the heterojunction between $Cd_{0.5}Zn_{0.5}S$ solid solutions and rGO. In addition, the heterojunction between CdS and ZnS was able to effectively promote electrons transfer from $Cd_{0.5}Zn_{0.5}S$ to rGO. However, most of these systems based on rGO/semiconductor must be further enhanced H_2 production activity from the perspective of practical application [30–32].

Another effectual strategy to further improve hydrogen evolution is to coupling appropriate cocatalysts with photocatalysts to decrease the recombination of electron-hole pairs. Considering high cost of the extensively investigated noble metal, it is quite worthwhile to search noble-metal free and earth abundance cocatalysts to further enhance the hydrogen-production activity. It is interesting to note that MoS_2, an earth-abundant layered transition metal sulfide, has been investigated as a promising cocatalysts for the hydrogen evolution [33,34]. MoS_2 has sandwich structure of three atom layers (S–Mo–S) stacking together by weak van der Waals forces [35,36]. Density functional calculations found that the free energy of atomic hydrogen surface bonding to the MoS_2 was almost zero, which is similar to that of Pt [30,37]. Moreover, previous studies have revealed that layered MoS_2 with superior H_2 activation performance of rich active edge sites from the S atoms is a more active and predominant cocatalyst than many noble metals. Xu [38] et al. has prepared a series of MoS_2/CdS photocatalysts that the 0.2 wt% MoS_2/CdS catalyst has been proved a higher efficiency than 0.2 wt% Pt/CdS. Wei [39] and his colleagues find $MoS_2/ZnIn_2S_4$ composite photocatalyst exhibits excellent promoting effect for H_2 production under visible light, it can be ascribed to the defect sites on the surface of MoS_2 that can act as adsorption sites for hydrogen evolution. Therefore, MoS_2 is a promising efficient and economic cocatalyst for hydrogen production [39–42].

Our previous study showed that among $Cd_{1-x}Zn_xS$ solid solutions, without noble metal loading, the PSGM/5.0%rGO/$Cd_{0.6}Zn_{0.4}S$ showed the highest H_2 production rate (unpublished). Therefore, 5.0%rGO/$Cd_{0.6}Zn_{0.4}S$ solid solution was used as model photocatalyst to prepare MoS_2/rGO/$Cd_{0.6}Zn_{0.4}S$ in this paper. Herein, a series of MoS_2/$Cd_{0.6}Zn_{0.4}S$ photocatalysts were synthesized on the surface of rGO/PSGM organic microspheres by a simple one-pot solvothermal reaction to enhance photocatalytic activity. The MoS_2 modified graphene-$Cd_{0.6}Zn_{0.4}S$ structure not only inhibits the aggregation of $Cd_{0.6}Zn_{0.4}S$ nanoparticles, but also assistants to overcome the poor conductivity of MoS_2. The conclusion showed that the hydrogen production activity of the rGO/$Cd_{0.6}Zn_{0.4}S$ can be improved about 2.1 times by loading MoS_2 and the stability can also be significantly enhanced at least 15 h. What's more, the catalytic rate of 5.0%MoS_2/rGO/$Cd_{0.6}Zn_{0.4}S$ active ingredients is 40.39 mmol/h/g, which is 14 times higher than the sample without PSGM organic microspheres.

Materials and methods

Materials

Crystalline flake graphite was purchased from Nanjing Yokook Nano Technology Co., Ltd. $(CH_3COO)_2Cd\cdot 2H_2O$, $(CH_3COO)_2Zn\cdot 2H_2O$, Dimethyl sulfoxide (DMSO), 2-methylpropionitrile (AIBN), and Potassium Permanganate ($KMnO_4$) were purchased from Adamas Reagent Co., Ltd. L-Cysteine and Styrene were both purchased from Shanghai Macklin Biochemical Co., Ltd. Sodium molybdate was purchased from Jiuding chemical (Shanghai) Technology Co., Ltd. Polyvinyl pyrrolidone (PVP), Concentrated sulfuric acid and Phosphoric acid were all purchased from Sinopharm Chemical Reagents Co., Ltd. All reagents are analytical grade, only AIBN was purified in ethanol and styrene was refined by a basic alumina column, the rests used as received without further purification.

Preparation of graphene oxide/styrene/glycidylmethacrylate microspheres (GO/PSGM)

Graphene oxide (GO) was synthesized from Graphite flakes according to an improved Hummers' method [43]. The organic polymer microspheres (PSGM) were prepared through dispersion polymerization method according to our previous study [44], and the best coating amount on the organic microspheres of graphene oxide was 5%wt. 10 mg GO and 200 mg amine-functionalized microspheres dispersed in 60 mL deionized water, the mixture kept 4 h in water bath at 343 K with stirring. After reaction, the products cooled down to the room temperature and collected by centrifugation, then washed with distilled water and ethanol alternately until the supernatant was colorless, residual solid materials dried overnight under room temperature.

Preparation of transition metal sulfide-modified rGO/$Cd_{0.6}Zn_{0.4}S$ photocatalyst

The MoS_2-modified rGO/$Cd_{0.6}Zn_{0.4}S$ photocatalyst were prepared via a facile hydrothermal method. Firstly, 200 mg 5%GO/PSGM microspheres, $Cd(OAc)_2\cdot 2H_2O$ and $Zn(OAc)_2\cdot 2H_2O$ in 3:2 M ratios were dissolved in 60 mL aqueous solution, the total

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