



Omnidirectional enhancement of photocatalytic hydrogen evolution over hierarchical “cauline leaf” nanoarchitectures



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ABSTRACT

The scrupulous design and integration of multiple active materials into hierarchical nanoarchitectures is essential for the creation of photocatalytic hydrogen evolution reaction (HER) system that can mimic natural photosynthesis. Here we report the design and preparation of a “cauline leaf”-like structure for highly efficient HER, by decorating TiO₂ nanofibers with vertical arrays of atomically-thin MoS₂ nanosheets and CdS nanocrystals. The unique integrated “cauline leaf” design can promote light trapping and absorption for highly efficient light harvesting and photocarrier generation, and offer unblocked electron transport pathway for rapid charge separation/transport to suppress charge recombination, as well as high surface area and high density of active sites for highly efficient utilization of photo-generated carriers for productive HER. Structural characterizations by transmission electron microscopy show well-integrated nanoarchitectures. Significantly, photocatalytic studies demonstrate rapid HER rates as high as 12.3 or 6.2 mmol h⁻¹ g⁻¹ under simulated solar light or visible light irradiation, with apparent quantum efficiencies of 70.5% at 365 nm or 57.6% at 420 nm, and excellent long term stability, representing one of the best reported MoS₂ hybrid HER photocatalysts. The study could open new opportunities for the rational design of nanoscale architectures for HER or other application.

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1. Introduction

Hydrogen energy is a promising alternative form of clean energy in the future. Loading of noble metal co-catalysts on semiconductors is an attractive way for photocatalytic production of molecular hydrogen, but are severely limited by their scarcity and cost for practical applications [1–3]. Tremendous efforts in recent years have proved that molybdenum disulfide (MoS₂) is a potential substitute for platinum [4–6]. The edge sites of MoS₂ nanosheets have been revealed to be the active sites for the hydrogen evolution reaction (HER) [7–9]. Generally, the main challenge in heterogeneous photocatalysis toward HER is to minimize the non-productive recombination and efficiently extract the photogenerated charges for productive hydrogen generation. To this end, a close integration of the semiconductor light har-

vesting antenna and hydrogen evolution cocatalysts is essential for ensuring efficient photocharge generation, separation, transport and utilization [10–13]. In particular, when MoS₂ nanosheets are used as the cocatalyst, not only the highly intimate interfacial contact between MoS₂ and semiconductor is required for the fast separation and transfer of photogenerated charges, but also the catalytically active edge sites of MoS₂ nanosheets in hybrid photocatalysts should be fully exposed for efficient HER [14–16]. Frustratingly, unshackled two dimensional transition-metal dichalcogenide nanosheet-based hybrids in solution tend to aggregate, greatly obstructing the exposure of edge active sites [17,18]. The scrupulous design and hybridization of MoS₂-based architectures are crucial to HER.

Although considerable efforts have been placed in preparing MoS₂ nanosheet-based hybrid photocatalysts [19–22], these pioneering studies are mostly focusing on the simple hybridization of MoS₂ nanosheets, without sufficient control of the nanoscale architectures for optimized performance [14]. On the other hand, it is expected that the HER performance of the catalysts is strongly dependent on their composition, crystal phase and structure, as well as the spatial organization/assembly of components. It is

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therefore highly desirable to prepare well-defined MoS₂ hybrid catalysts in a highly controllable fashion [14,23,24].

Here we report the rational design and synthesis of a “cauline leaf”-like structure for highly efficient HER, by decorating 1D TiO₂ nanofibers with a vertical array of atomically-thin 2D MoS₂ nanosheets and 0D CdS nanocrystals (TiO₂@MoS₂@CdS) (Scheme 1). 1D TiO₂ nanofibers have been saved as an ideal scaffold to composite with other homogeneous or heterogeneous MoS₂ nanosheets in order to ensure high surface area, reinforce light scattering and trapping, and suppress unexpected back reaction (charge recombination). 0D CdS nanocrystals anchored on the 2D MoS₂ nanosheets serve as the photocenter for efficiently harvesting solar light to generate charge carriers. The 0D/1D/2D hierarchical nanoarchitectures fully integrate the merits and mitigate the drawbacks of the single units. Such a hierarchical “cauline leaf” architecture maximizes omnidirectional enhancement in photocatalytic hydrogen evolution. These results show the importance of morphology control in the preparation of base MoS₂ as cocatalyst for highly efficient photocatalytic hydrogen evolution.

2. Experimental

2.1. Materials

Poly(vinylpyrrolidone) (PVP, Mw = 1,300,000) was purchased from Alfa Aesar. All other reagents and materials were obtained commercially from the Beijing Chemical Reagent (Beijing, China) and used as received without further purification.

2.2. Synthesis of porous electrospun TiO₂ nanofibers

Typically, 0.45 g of PVP was dissolved in 3 mL ethanol with vigorous stirring for 1 h. 1.5 g of titanium tetraisopropoxide (Ti(O_iPr)₄) was dissolved in a mixture of 3 mL ethanol and 3 mL acetic acid by stirring for 1 h to obtain a homogeneous precursor solution, and then the above PVP solution was added to the homogeneous precursor solution, followed by vigorous stirring for 3 h. The mixed solution was put into a syringe for electrospinning. An electrical potential of 10 kV was applied at an electrode distance of 15 cm. The mixed solution was ejected at a rate of 0.5 mL h⁻¹, resulting in electrospun nanofibers. The as-collected nanofibers were calcined at 450 °C for 2 h in air atmosphere to remove PVP with the formation of TiO₂ crystals. PVP acted as here both linkers between the inorganic precursors to facilitate electrospinning and porogenic agents to obtain porous TiO₂ nanofibers after the PVP removal by a calcination process.

2.3. Preparation of TiO₂@MoS₂ heterostructures

The formation process of TiO₂@MoS₂ heterostructures was described below: typically, 45 mg sodium molybdate (Na₂MoO₄·2H₂O) and 90 mg thioacetamide (C₂H₅NS) were dissolved in 20 mL deionized water to form a transparent solution. Then 20 mg calcined TiO₂ nanofibers were added into the above solution and stirred to get a suspension. The suspension was transferred to a Teflon-lined stainless steel autoclave and then heated in an electric oven at 220 °C for 24 h. The solid product was dried at 80 °C for 12 h to obtain TiO₂@MoS₂ heterostructures (containing 60 wt% of MoS₂). The content of MoS₂ in TiO₂@MoS₂ could be tuned by adjusting the amount of Na₂MoO₄·2H₂O and C₂H₅NS precursors, and only the optimized TiO₂@MoS₂ sample containing 60 wt% of MoS₂ was used for analysis in detail unless otherwise stated. For comparison, pure MoS₂ nanosheets were prepared under the same conditions without TiO₂ nanofibers.

2.4. Synthesis of TiO₂@MoS₂@CdS heterostructures

In a typical synthesis process of TiO₂@MoS₂@CdS, 50 mg TiO₂@MoS₂ was dispersed in 50 mL aqueous solution containing 138.38 mg Cd(AC)₂·2H₂O by sonication for 8 h. Then 0.05 M Na₂S·9H₂O was added at the rate of 0.05 mL/min and continuously stirred for 24 h. Finally, the products were washed with distilled water and dried in air at 60 °C. The content of CdS in TiO₂@MoS₂@CdS was tuned by the amount of raw materials. For comparison, pure CdS nanoparticles were prepared by adding sodium sulfide (10 mL, 0.1 mm) to cadmium acetate (10 mL, 0.1 mm) with stirring; the precipitate formed was centrifuged and dried at 60 °C. For comparison, TiO₂@CdS was prepared under the same conditions without MoS₂ nanosheets.

2.5. Characterization

The morphologies and microstructures of the samples were characterized using an S-4800 field emission scanning electron microscope (FESEM, Hitachi, Japan) and a transmission electron microscope (TEM, JEOL JEM-2100F). The EDS mapping images were captured on a Tecnai G2 F20 S-TWIN atomic resolution analytical microscope. The crystal phases of the samples were collected on an X-ray diffractometer with Cu-Kα radiation (XRD, M21X, MAC Science Ltd., Japan). The binding energies of S, Mo, and O of the heterostructures were determined by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher Scientific, England) using an Al-Kα X-ray source. The UV–vis diffuse reflectance spectra (DRS) were performed on a UV–vis spectrophotometer (Cary 300, USA) with an integrating sphere. The photoluminescence (PL) spectra for solid samples were investigated through F-7000. The time-resolved transient photoluminescence (TRPL) spectrum was performed using Hamamatsu universal streak camera C10910. The BET specific surface areas were measured on Belsorp-Mini II analyser (Japan).

2.6. Photoelectrochemical measurements

The photoelectrochemical responses of the samples were carried out with a CHI 660C electrochemical analyzer (CHI Inc., USA) in a three-electrode configuration. FTO electrodes deposited with the samples as a photoanode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All the samples were analyzed under room temperature without bias potential. 0.35 M/0.25 M Na₂S–Na₂SO₃ aqueous solution was used as the electrolyte. For the fabrication of the photoanode, 0.25 g of the sample was grinded with 0.06 g polyethylene glycol (PEG, molecular weight: 20000) and 0.5 mL ethanol to make a slurry. Then, the slurry was coated onto a 1 cm × 4 cm F-doped SnO₂-coated glass (FTO glass) electrode by the doctor blade technique, and then allowed to dry in air. A 300 W xenon arc lamp with lighting wavelength range of 320–780 nm (Perfectlight, PLS-SXE 300C, Beijing, China) was used as light source. The light intensity parameters are provided by Beijing Perfectlight Technology Co., Ltd. (see Fig. S1 in Supporting information). The incident light intensity was 160 mW cm⁻² measured by a radiometer (FZ-A, Photoelectric Instrument Factory of Beijing Normal University, China).

2.7. Photocatalytic hydrogen production tests

The photocatalytic hydrogen evolution experiments were performed in a 100 mL sealed quartz flask at ambient temperature and atmospheric pressure. A 300 W xenon arc lamp with lighting wavelength range of 320–780 nm (Perfectlight, PLS-SXE 300C, Beijing, China) was used as light source to trigger the photocatalytic reaction. The lamp was positioned 10 cm away from the reactor

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