Journal of Catalysis 352 (2017) 35–41

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

A novel hybrid artificial photosynthesis system using MoS_2 embedded in carbon nanofibers as electron relay and hydrogen evolution catalyst

Fujun Niu [a,#], Chung-Li Dong [b,#], Changbao Zhu [e,#], Yu-Cheng Huang [d], Miao Wang [a], Joachim Maier [e], Yan Yu [c,*], Shaohua Shen [a,f,*]

[a] International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, 28 West Xianning Road, Xi'an, Shaanxi 710049, China
[b] Department of Physics, Tamkang University, 151 Yingzhuan Rd., New Taipei City 25137, Taiwan
[c] State Key Laboratory of Fire Science and Key Laboratory of Materials for Energy Conversion, Chinese Academy of Sciences (CAS), Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China
[d] Department of Electrophysics, National Chiao Tung University, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan
[e] Max Planck Institute for Solid State Research, Heisenbergstr. 1, Stuttgart 70569, Germany
[f] Xi'an Jiaotong University Suzhou Academy, Suzhou, Jiangsu 215123, China

ARTICLE INFO

Article history:
Received 23 March 2017
Revised 24 April 2017
Accepted 24 April 2017
Available online 25 May 2017

Keywords:
Artificial photosynthesis
MoS_2
Carbon nanofibers
Hydrogen generation

ABSTRACT

Inspired by photosynthesis in nature, artificial photosynthesis (AP) systems have been widely investigated in the context of energy and environmental research. Here we report a noble-metal-free AP system for visible-light-driven H_2 generation from aqueous solutions consisting of fluorescein (FL) as photosensitizer, single-layer ultrasmall MoS_2 nanoplates embedded in carbon nanofibers (CNF) as electron relay and redox catalyst, and triethanolamine (TEOA) as sacrificial electron donor. This CNF–MoS_2/FL system exhibits outstanding H_2 evolution performance, with an H_2 generation rate that exceeds not only both MoS_2/FL (by 100%) and CNF/FL (by 1100%), but also the Pt/FL system (by 40%). The excellent photocatalytic activity of this CNF–MoS_2/FL system can be ascribed to the synergistic effects of CNF and MoS_2 coupling: (1) the simultaneous presence of MoS_2 with its delocalized and increased Mo 4*d* unoccupied states and of CNF with increased graphitic characteristics enables electron transfer from FL* to MoS_2 via CNF electron relay; (2) the single-layered ultrasmall MoS_2 nanoplates with short effective lengths for electron transfer and high density of reactive S-edges effectively catalyze the H_2 evolution reaction (HER). The presented work successfully fabricated a highly efficient AP system for solar H_2 production from a fully aqueous solution and indicated CNF–MoS_2 as a promising candidate to replace Pt for solar fuel conversion.

1. Introduction

Artificial photosynthesis (AP) systems containing a photosensitizer (PS) and a redox catalyst to split water into hydrogen are not only attractive research objects for mitigating energy and environmental problems, but also very challenging ones [1–3]. As PSs for AP systems, molecular dyes are candidates of choice due to their atom-level adjustment of structures and physicochemical properties [4–6]. Among these molecular dyes, inexpensive dyes (e.g., xanthene and porphyrin-derived molecules) are targeted rather than the widely used noble-metal-based complexes (e.g., Ru- and Ir-based molecules) [4,7].

In AP systems with molecular dyes as PSs, electron relays are needed to reduce the energy-wasting electron back transfer by bimolecular quenching of the excited photosensitizer (PS*) to transfer electrons to the catalyst for H_2 generation [8,9]. Compared with the widely used organic electron relays (e.g., methyl viologen and $Rh^{III}(bpy)_2Cl_3$), inorganic nanomaterials, such as carbon nanotubes [10], graphene [11], TiO_2 [12], and carbon nanofibers [13], are expected to do good service as electron relays for stability and abundance reasons. Of particular interest are carbon nanofibers (CNF) [14], popular carbon materials with superior electron mobility and high surface-to-volume ratio. For example, Ding et al. reported that CNF could greatly improve the electrocatalytic

---

* Corresponding authors at: State Key Laboratory of Fire Science and Key Laboratory of Materials for Energy Conversion, Chinese Academy of Sciences (CAS), Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China (Y. Yu). International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, 28 West Xianning Road, Xi'an, Shaanxi 710049, China (S. Shen).

E-mail addresses: yanyumse@ustc.edu.cn (Y. Yu), shshen_xjtu@mail.xjtu.edu.cn (S. Shen).

[#] These authors contributed equally.

http://dx.doi.org/10.1016/j.jcat.2017.04.027
0021-9517/

activity of a Ni catalyst due to intimate interactions and efficient charge transport between CNF and Ni [15].

In the past few decades, numerous efforts have been made to develop versatile catalysts for the hydrogen evolution reaction (HER) [3,16,17]. Among these catalysts, the noble metal Pt is widely used and shows very high activity [18]. However, its scarcity and high cost preclude upscaling [19]. Therefore, it is of great urgency to develop cheap and earth-abundant catalysts which are stable and efficient for HER. In recent years, a number of non-precious-metal catalysts have been developed for solar H_2 evolution [20], such as transition metal oxides, sulfides, and nitrides. Among these noble-metal-free catalysts, MoS_2 has been widely employed for photocatalytic and electrocatalytic HER due to its extraordinary physicochemical properties, including low overpotential and highly active exposed S-edges [21]. However, it has always suffered from stacking and aggregation through π–π interaction in the synthesis process due to its layered structure and high surface energy, leading to blocked catalytic S-edge sites, high resistance for electron transfer, and lowered catalytic activity [22]. In addition, the conductivity of MoS_2 is relatively poor, hindering electron transfer to the S-edges for surface reactions [11]. The ideal system to overcome these obstacles would use small and single-layered MoS_2 with very high surface-to-volume ratios and a high density of S-edge active sites, which are coupled with electronic conductive phases (e.g., carbon materials and Au). Moreover, both the synthesis method and the material should be simple and cheap for potential upscaling. Recently, Zhu et al. [23] have reported a simple and inexpensive electrospinning method to prepare single-layered ultrasmall MoS_2 nanoplates embedded in CNF, which is worth investigating, as it meets these criteria.

Here, an inexpensive AP system is reported, which contains fluorescein (FL) as the PS, single-layered ultrasmall MoS_2 nanoplates embedded in CNF (CNF-MoS_2) as electron relay and redox catalyst, and triethanolamine (TEOA) as sacrificial electron donor for visible-light-driven H_2 generation from a fully aqueous solution. This CNF–MoS_2/FL system exhibits outstanding HER activity, exceeding that of the CNF/FL and the MoS_2/FL system by 1100% and 100%, respectively, and better than that of the Pt/FL system (140%). We ascribe the impressive photocatalytic activity of this CNF–MoS_2/FL system to the properties of the MoS_2 nanoplates and the coupling with CNF: (1) the combination of MoS_2 with its delocalized and increased Mo 4*d* unoccupied states and of CNF with its graphitic conductivity characteristic favor electron transfer from photoexcited FL^* to MoS_2; (2) the single-layered ultrasmall MoS_2 nanoplates themselves catalyze HER due to the short effective electron transfer length and the reactive S-edges. The present study demonstrates a highly efficient noble-metal-free AP system for visible-light-driven H_2 generation and proposes CNF–MoS_2 as a promising and low-cost candidate for designing an efficient AP system for solar H_2 production.

2. Experimental

2.1. Preparation of CNF–MoS_2, CNF, and MoS_2 catalysts

All the chemicals were of analytical grade and used as received except as noted. CNF–MoS_2 was synthesized according to the literature [23]. Typically, N,N-dimethylformamide (DMF) was dissolved with $(NH_4)_2MoS_4$ (0.2 mol/L) and polyvinylpyrrolidone (PVP, Mv = 1,300,000 g/mol) (8 wt.%). Then the solution was transferred into a syringe equipped with a metal needle of diameter 1.6 mm. To collect the nanowires, a grounded stainless steel plate was placed 15 cm below the spinneret and the flow rate was kept at 15 μmol/min. A high-voltage power supply (Model HCE35-35000, FUG DC power source, Germany) was employed at 20 kV. With a heating rate of 1 °C/min, the obtained electrospun fiber was calcined using a tube furnace at 450 °C for 2 h under H_2 (5 vol.%)/Ar (95 vol.%) and then at 800 °C for 6 h under Ar to obtain the final product. The MoS_2 content of CNF–MoS_2 was about 62 wt.%, as reported in our previous work [23] (see detailed discussion in the Supplementary Information). CNF was prepared in the same way as CNF–MoS_2 except for the addition of $(NH_4)_2MoS_4$.

MoS_2 as control sample was prepared by an ultrasound-assisted hydrothermal method as reported elsewhere in the literature, with some modification [22,24]. Typically, 0.7427 g of ammonium molybdate and 1.3702 g of thiourea were added to 60 mL of water and stirred for 1 h. Then the obtained solution was transferred into a 100 mL Teflon-lined autoclave and kept at 220 °C for 18 h. After the solution was cooled, the solid product was collected by centrifugation (10,000 rpm/min for 10 min), washed with water several times, and then dispersed in water for ultrasonic treatment for 2 h. Then the suspension was centrifuged at 1000 rpm for 2 min to get the supernatant. The obtained supernatant was further centrifuged at 10,000 rpm for 10 min and dried at 60 °C for 12 h in a vacuum oven to get the final product.

2.2. Preparation of CNF, MoS_2, Pt, and CNF–MoS_2 films

CNF, MoS_2, and CNF–MoS_2 films were prepared by a drop-coating method. Typically, 10 mg of catalyst and 200 μL of Nafion (0.5 wt.%) were ultrasonically dispersed in 2.5 mL of water/ethanol (4:1) mixed solvents. Then a certain amount of the dispersion was drop-cast onto the fluorine-doped SnO_2 (FTO) substrate and put on a heating plate. The prepared working electrode was further dried at 60 °C for 10 h in a vacuum oven. Pt film was prepared by sputtering Pt onto the surface of the FTO substrate using a JFC-1600 auto fine coater.

2.3. Characterization

Crystal structures of CNF, MoS_2, and CNF–MoS_2 were recorded by a powder X-ray diffractometer (X'Pert PRO MPD, PANalytical, the Netherlands) using Cu Kα radiation in the range $2\theta = 10$–$80°$ (XRD). UV–vis diffuse reflectance spectra of the solutions were detected by a Hitachi U-4100 UV–vis–near IR spectrophotometer with the corresponding blank aqueous solution as the reference. Photoluminescence (PL) emission spectra were recorded using a PTI QM-4 fluorescence spectrophotometer. The catalyst was ultrasonically dispersed in ethanol and then, by a dipping and drying process, deposited on copper grids for transmission electron microscopy (TEM) analysis (G2 F30, FEI, USA). The morphology of the samples was observed by a field emission scanning electron microscope (SEM, JEOL JSM-7800F) operated at 3.0 kV. Synchrotron X-ray spectroscopy tests at the C *K*-edge, S *K*-edge, and Mo *L*-edge were conducted at BL20A at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan.

2.4. Photocatalytic hydrogen production

The photocatalytic hydrogen evolution tests were performed in a gas-closed circulation system containing a 115 mL Pyrex glass cell as the photoreactor. The reaction temperature was maintained at around 35 °C by thermostatic circulating water. The light source was a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Technology Co., Ltd., China) with a UV cutoff filter (>420 nm). Hydrogen gas was detected by a gas chromatograph (GC, SP-2100, Beijing Beifen-Ruili Analytical Instrument Co., Ltd, China) with N_2 as carrier gas. In a typical experiment, a certain amount of catalyst was ultrasonically dispersed into 80 mL of aqueous solution containing a certain amount of FL and 8 mL of triethanolamine (TEOA). Then the suspension was purged using N_2 for 30 min to remove air before irradiation. Control experiments showed that no H_2 evolu-