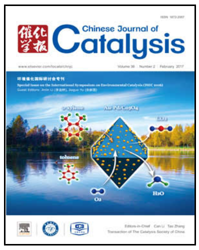
Chinese Journal of Catalysis 38 (2017) 313–320

available at www.sciencedirect.com

ScienceDirect

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



Article (Special Issue on the International Symposium on Environmental Catalysis (ISEC 2016))

Three-dimensional MoS_2/reduced graphene oxide aerogel as a macroscopic visible-light photocatalyst

Ruiyang Zhang [a], Wenchao Wan [a], Dawei Li [a], Fan Dong [b], Ying Zhou [a,*]

[a] *State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, Sichuan, China*

[b] *Chongqing Key Laboratory of Catalysis and Functional Organic Molecules, College of Environmental and Biological Engineering, Chongqing Technology and Business University, Chongqing 400067, China*

A R T I C L E   I N F O

Article history:
Received 29 August 2016
Accepted 26 September 2016
Published 5 February 2017

Keywords:
Molybdenum disulfide/reduced graphene oxide aerogel
Composite
Photocatalysis
Visible light
Adsorption

A B S T R A C T

Photocatalysis is regarded as an ideal technology for solving the urgent environmental and energy issues that we face today. Among the reported photocatalysts, molybdenum disulfide (MoS_2) is very promising for applications in hydrogen production and pollutant photodegradation. However, its lack of active sites and the difficulty of recovering catalysts in powder form have hindered its wide application. Here, we report the successful preparation of a macroscopic visible-light responsive MoS_2/reduced graphene oxide (MoS_2/RGO) aerogel. The obtained MoS_2/RGO aerogel exhibits enhanced photocatalytic activity towards hydrogen production and photoreduction of Cr(VI) in comparison with the MoS_2 powder. In addition, the low density (56.1 mg/cm^3) of the MoS_2/RGO aerogel enables it to be used as an efficient adsorption material for organic pollutants. Our results demonstrate that this very promising multifunctional aerogel has potential applications in environmental remediation and clean energy production.

1. Introduction

Serious environmental pollution and the depletion of energy resources are two of the most urgent issues that we face today. Recently, two-dimensional layered materials have attracted worldwide attention in the environmental and energy fields owing to their unique properties and numerous potential applications [1]. Among them, MoS_2 is a semiconductor with a tunable bandgap that depends on the number of MoS_2 layers. Theoretically, the bandgap of bulk MoS_2 is 1.2 eV, whereas that of monolayer MoS_2 is 1.9 eV [2]. MoS_2 can be used in a very wide range of applications, such as solid lubricants [3], electrocatalysts for hydrogen evolution [4], and energy storage for batteries and supercapacitors [5]. Each layer of MoS_2 has a sandwich structure with strong covalent bonding between the Mo and S atoms. However, the weak inter-layer binding allows other molecules to insert between the MoS_2 layers, resulting in materials with fascinating properties [6]. MoS_2 has also been considered as an alternative co-catalyst to the noble metal platinum because of its low cost and conduction band (CB) edge potential (−0.1 eV) that allows electrons from another semiconductor to be transferred to MoS_2 and enhance electrical transport [7]. Nevertheless, both theory and experiment have demonstrated that only the edge sites of MoS_2 are catalytically active. In addition, the fast recombination of the photo-generated charge carriers in MoS_2 further limits its application as a

* Corresponding author. Tel: +86-28-83037411; Fax: +86-28-83037406; E-mail: yzhou@swpu.edu.cn
This work was supported by the National Natural Science Foundation of China (U1232119, 21403172), the Sichuan Youth Science and Technology Foundation (2013JQ0034, 2014JQ0017), and the Innovative Research Team of Sichuan Province (2016TD0011).
DOI: 10.1016/S1872-2067(16)62568-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 2, February 2017

photocatalyst [8]. Many studies have been conducted to overcome these bottlenecks, for example through the fabrication of defect-rich MoS_2 ultrathin nanosheets [9] and hybrids of MoS_2 with platinum [10], graphene [11], polyaniline (PANI) [12], or other highly conductive materials. Gao et al. [12] developed PANI-modified three-dimensional (3D) flower-like MoS_2, which exhibited enhanced adsorption and photoreduction of Cr(VI). Chang et al. [13] demonstrated that the S atoms on the exposed edge sites played an important role in the adsorption of H^+, and allowed the reduction from H^+ to H_2. However, these improvements are primarily applied to MoS_2 in powder form, which is not only difficult to recover, but also has a strong tendency to agglomerate [14]. Hence, the fabrication of a macroscopic MoS_2 photocatalyst remains a great challenge.

Graphene aerogel (GA), which has a low density, large surface area, and high porosity, has received enormous attention as a supercapacitor, catalyst support, and adsorbent material [15,16]. Importantly, GA could act as an ideal scaffold for catalysts owing to its porous 3D network structure and multi-dimensional electron transport pathways [8]. Considerably enhanced photocatalytic activity has been observed after coupling photocatalysts with GA or its derivatives, reduced graphene oxide (RGO) and graphene oxide (GO) aerogels. Liu et al. [17] reported a facile hydrothermal method for the preparation of TiO_2/GA, which can photocatalytically degrade various pollutants. Fan and co-workers [18] demonstrated that AgBr and AgCl showed an enhanced photocatalytic performance when grown on the surface of GA. In our previous work, we revealed that macroscopic C_3N_4/GO aerogel photocatalysts with various sizes and shapes could be fabricated through a cost-effective freeze-casting process [19]. Nevertheless, to the best of our knowledge, there is no research reporting photocatalytic H_2 production and photoreduction of Cr(VI) using a macroscopic MoS_2 aerogel photocatalyst.

In the present work, we report a facile method for the fabrication of a macroscopic MoS_2/RGO aerogel photocatalyst using a hydrothermal method followed by freeze-drying. The obtained MoS_2/RGO aerogel exhibited considerably enhanced photocatalytic activity towards both photocatalytic H_2 production and photoreduction of Cr(VI) compared with the MoS_2 powder. In addition, owing to the low density (56.1 mg/cm^3) of the MoS_2/RGO aerogel, adsorption capacities of 10–20 times the weight of the aerogel sample could be achieved, depending on the density of the adsorbed organics.

2. Experimental

2.1. Materials

Natural graphite flakes (32 mesh) were purchased from Qingdao Jin Ri Lai Graphite Co., Ltd. Other reagents were purchased from Chengdu Kelong Chemical Co., Ltd. All reagents were of analytical grade and used without further purification.

2.2. Preparation

MoS_2 powder was prepared via a hydrothermal method. In a typical synthesis, 106 mg ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and 1 g thiourea ($CS(NH_2)_2$) were placed in a 25 mL Teflon-lined stainless steel autoclave containing 15 mL deionized water. After stirring for 30 min, the autoclave was heated at 180 °C for 24 h and then cooled naturally to room temperature. The final black powder was washed several times with deionized water and ethanol and dried at 60 °C. GO was prepared using a modified Hummers method as described in our previous work [15,16]. The final concentration of the GO solution was 3 mg/mL.

For the preparation of the MoS_2/RGO aerogel, 106 mg ammonium molybdate and 1 g thiourea were dispersed in 5 mL deionized water in a 25 mL Teflon-lined stainless steel autoclave under stirring. Then, 10 mL GO solution (3 mg/mL) and 40 μL ammonia were added. After stirring for 1 h, the autoclave was heated at 180 °C for 24 h and cooled naturally to room temperature. The obtained hydrogels were washed with deionized water and then frozen at −80 °C for 2 h. The MoS_2/RGO aerogel was produced after freeze-drying for 48 h. The weight ratio of MoS_2 to RGO was 7:3.

2.3. Characterization

Powder X-ray diffraction (XRD) was performed on a PANalytical X'pert diffractometer operated at 40 kV and 40 mA with Cu K_α radiation. The morphology and microstructure of the prepared samples were investigated by scanning electron microscopy (SEM) using a ZEISS EVO MA15 microscope and transmission electron microscopy (TEM) was performed on a FEI tecnai G2 F30 microscope. UV-vis-near infrared (NIR) spectroscopy was performed on a Shimadzu UV-2600 spectrophotometer. Fourier transform infrared spectra (FTIR) were recorded on a Thermo Nicolet 6700 spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific Escalab 250Xi spectrometer and the binding energy shifts were corrected using the C 1*s* signal at 284.6 eV. The specific surface area (SSA) was measured in suspension using UV-vis spectroscopy (UV-5100, Anhui Wanyi) with the methylene blue (MB) staining method [20] and calculated using the following equation:

$$SSA = N_A A_{MB}(C_0 - C_e)V/(M_{MB} m_s) \quad (1)$$

where N_A is Avogadro's number (6.02×10^{23} mol^{-1}), A_{MB} is the surface coverage per molecule of MB (typically 1.35 nm^2), C_0 and C_e are the initial and equilibrium concentrations of MB, respectively, V is the volume of the MB solution, M_{MB} is the molecular mass of MB, and m_s is the mass of the sample.

2.4. Photocatalytic activity and adsorption capacity measurements

Photocatalytic hydrogen evolution was determined using a 500 W high pressure Hg lamp (15.7 mW/cm^2) as the light source with a visible light filter (> 420 nm). The samples (5 mg) were dispersed in 10 mL of a mixed solution of sodium sulfide (0.1 mol/L) and sodium sulfite (0.6 mol/L) as a sacrificial agent system in a Pyrex tube. Ar was bubbled for 30 min to remove O_2 and 1 mL CH_4 gas was injected as an internal standard, and