

Regular Article

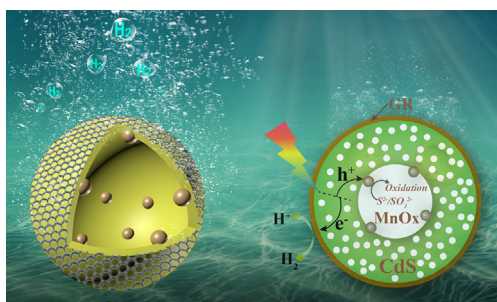
Manganese oxide at cadmium sulfide (MnOx@CdS) shells encapsulated with graphene: A spatially separated photocatalytic system towards superior hydrogen evolution

Pengfei Tan^a, Anquan Zhu^a, Lulu Qiao^a, Weixuan Zeng^a, Hao Cui^{b,*}, Jun Pan^{a,*}

^aState Key Laboratory for Powder Metallurgy, Central South University, Lushan South Road 932, Changsha 410083, PR China

^bSino-Platinum Metals Co. Ltd., Kunming Institute of Precious Metals, People West Road 121, Kunming 650106, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 June 2018

Revised 1 August 2018

Accepted 28 August 2018

Available online 29 August 2018

Keywords:

Spatially separated

MnOx@CdS

Graphene

Hydrogen evolution

Photocatalytic

ABSTRACT

Exploring novel, high-efficiency and durable catalysts is of vital importance to expedite current research on photocatalytic H₂ evolution and address the energy and environmental issues. Herein, we rationally designed and synthesized a novel MnOx@CdS@GR photocatalyst with spatially separated dual co-catalysts for efficient visible-light-driven hydrogen production activity. In this spatially separated photocatalytic system, reduced graphene oxide (GR) and MnOx nanoparticles were anchored on the outer and inner surfaces of CdS shells acting as electron and hole collectors, respectively. The composition, microstructure and optical properties of the samples were thoroughly investigated. Photoluminescence spectra and photocurrent response as well as electrochemical impedance spectra were employed to reveal the separation and transfer ability of photo-generated charge carriers in the spatially separated MnOx@CdS@GR catalyst. Benefit from the synergistic effect including boosted light absorption capacity, enlarged specific surface area and increased separation and transfer efficiency of electron/hole pairs, the MnOx@CdS@GR exhibited superior H₂ evolution performance, and the optimized H₂-evolution rate reached a value of 5.45 mmol h⁻¹ g⁻¹, which is approximately 7.2 times than that of bare CdS. Moreover, this novel catalyst also displayed a long-term stability without apparent debasement in H₂ evolution activity. Finally, the photocatalytic mechanism was proposed and discussed.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

Photocatalytic H₂ evolution from water splitting in the presence of solar light and semiconductor, which realizes the conversion of

* Corresponding authors.

E-mail addresses: cuihao@ipm.com.cn (H. Cui), jun.pan@csu.edu.cn (J. Pan).

solar energy to chemical energy, has received intensive attention due to the huge potential to address the current energy and environmental crises [1–4]. Ever since the innovative work on photocatalytic splitting water by TiO₂ electrodes was reported by Fujishima and Honda in 1972, numerous semiconductors such as oxide-, sulfide- and carbide-based materials, have been studied for photocatalytic H₂ generation [5–13]. Among the diverse semiconductor catalysts, CdS has attracted particular attention because of its narrow bandgap and sufficient conduction band potential to reduce H⁺ to H₂. Nevertheless, it suffers from poor H₂ production activity due to innate defects such as limited light-absorption range, rapid recombination of charge carriers and severe photocorrosion. To date, various strategies, including constructing heterojunction or Z-scheme [14,15], tailoring crystal phase and morphology [16,17], loading co-catalyst [18–20] and so on, have been developed to solve these defects and further improve its performance of H₂ evolution. Despite some achievements have been made, it is still desirable and urgent to exploit new, cheap and stable CdS-based materials with excellent photocatalytic activity.

Recently, spatially separated co-catalysts loaded onto the interior and exterior surface of catalyst seems to be a more fascinating way to suppress the charge recombination due to the completely opposite direction migration of electron-hole pairs [18,21–24]. In those spatially separated photocatalytic systems, reduction co-catalysts (Pt, Pd, etc.) and oxidation co-catalysts (MnOx, CoOx, etc.) were used as electron collectors and hole collectors, respectively. In such way, the electrons and holes can move to the opposite direction to achieve the purpose of outstanding charge separation ability. For example, Domen et al. successfully synthesized Ta₃N₅ core/shell photocatalyst loaded with Pt and CoOx nanoparticles onto the inner and outer surface of Ta₃N₅ shell to promote its H₂ evolution activity [22]. Gong et al. reported the fabrication of spatially separated Pt@TiO₂@MnOx photocatalyst with enhanced performance of H₂ generation, in which Pt and MnOx NPs were selectively loaded on the interior and exterior surface of TiO₂ shell [24]. These reports definitely proved more efficient separation of charge carriers was made through the spatially separated co-catalysts systems. In addition, we also note that overwhelming majority of electron collectors employed in those reported spatially separated systems are the noble metals such as Pt nanoparticles which unavoidably restricts their application due to the scarcity and costliness of noble metals. On the other hand, graphene, a two-dimensional (2D) single atomic layer of graphite, has been proved to be an excellent electron transporter and collector in previous works [25–32]. After modifying with graphene, those graphene-based nanocomposites displayed higher H₂ production activity than bare semiconductors due to enhanced light absorption, improved surface area, as well as accelerated charges separation and transfer. The exciting results were ascribed to the unique properties of graphene such as excellent electrical conductivity, superior electron mobility and large theoretical specific surface areas [33,34]. On account of these special characteristics, it has great potential to introduce graphene into the spatially separated photocatalytic systems as an alternative to noble metals.

Inspired by the above discussion, we herein designed and synthesized a spatially separated photocatalytic system composed of MnOx@CdS hollow spheres wrapped by GR (named MnOx@CdS@GR) to promote the H₂ evolution efficiency of CdS. In this composite catalyst, MnOx nanoparticles were loaded on the inner surface of CdS shell to act as hole collectors, while the outer shell surface was encapsulated with GR as electron transporter and collector. The spatially separated co-catalysts (MnOx and GR) could drive photo-excited holes and electrons in the surface of CdS to move in the opposite direction, thus facilitating their separation. In combination with other advantages, such as

enhanced light harvesting and increased surface area, the MnOx@CdS@GR exhibited superior H₂ evolution performance under visible light irradiation.

2. Experimental section

2.1. Materials

All reagents in this work were used as-received and without further purification.

2.2. Synthesis of graphene oxide (GO)

GO was prepared according to a modified Hummers' method [35], which was also used in our previous work [36].

2.3. Synthesis of MnOx@CdS

MnOx@CdS was prepared by employing SiO₂ nanospheres as templates [18]. The typical process is described in the [Supporting Information](#) in detail.

2.4. Synthesis of MnOx@CdS@GR

The MnOx@CdS@GR nanocomposites were synthesized by a facile and efficient electrostatic self-assembly process between MnOx@CdS and GO, followed by chemically reduction of GO in the presence of hydrazine. Typically, the process mainly contains three steps: (I) The obtained MnOx@CdS nanospheres were firstly dispersed in 150 mL ethanol by sonication for 30 min. Afterwards, 2 mL of APTES was added to the abovementioned solution and refluxed at 80 °C for 4 h. Then, the products were centrifuged and washed with ethanol followed by dried at 60 °C in a vacuum oven to obtain amine-functionalized MnOx@CdS nanospheres. (II)

The aforementioned APTES-treated MnOx@CdS nanospheres were dispersed in distilled water with sonication for 30 min. Then a negatively charged GO suspension (0.2 mg/mL) was added to the aforesaid MnOx@CdS dispersion with the weight ratio of GO to MnOx@CdS at 0.05:1 under mild stirring at room temperature. (III) After being stirred for 2 h, hydrazine solution (50% in water, the weight ratio of hydrazine to graphene oxide is about 7:10) was added to the above-mentioned suspension drop by drop in order to achieve chemical conversion of GO to GR and obtain GR wrapped MnOx@CdS (called MnOx@CdS@GR). Finally, the resulting products were washed with deionized water four times, and then freeze dried. The real weight ratios of MnOx and GR in the sample of MnOx@CdS@GR were listed in [Table S1](#).

2.5. Characterization of catalysts

Zeta potential measurements of the samples were performed using a Zeta Potential Analyzer (Zetasizer Nano ZS). The phase structures were analyzed by X-ray diffraction (D/max 2550, Rigaku Corporation). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB250 X-ray photoelectron spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded on a BRUKER TENSOR 27 spectrometer. The Raman data of powder samples were acquired on a LabRAM HR Raman microscope equipment. The morphology of the catalysts was characterized using field emission transmission electron microscopy (JEM-2100F, JEOL). Elemental analyses were tested by using an elemental analyzer (VARIO EL111) attached to TEM. The surface area was determined by the Brunauer-Emmett-Teller (BET) method on a BK132F surface area analyzer. UV–vis diffuse reflection spectra were carried out with a UV–vis spectrophotometer using BaSO₄ as the standard reference (Evolution 220, Thermo Fisher Scientific).

Download English Version:

<https://daneshyari.com/en/article/10133177>

Download Persian Version:

<https://daneshyari.com/article/10133177>

[Daneshyari.com](https://daneshyari.com)